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PRECIPITATION OF GOLD AND SILVER FROM CYANIDE SOLUTION ON CHARCOAL

BY

JOHN GROSS and J. WALTER SCOTT

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PRECIPITATION OF GOLD AND SILVER FROM CYANIDE SOLUTION ON CHARCOAL

By John Gross and J. Walter Scott

INTRODUCTION

In its endeavor to increase efficiency in the production and treatment of mineral substances the Bureau of Mines has studied various problems of the metallurgy of the precious metals. This paper deals with a possible improvement in the cyanidation of gold and silver ores.

Charcoal is a strange and interesting substance. The fact that it has the power to abstract gold and silver from cyanide solutions to the extent of 7 per cent of its weight in gold and 3 per cent of its weight in silver without showing the slightest change in appearance, even under the microscope, clothes it with a mystery that has long interested metallurgists. Even now, with the mass of data made available by various investigators, much remains to be learned. At present, charcoal adsorption is being studied by many persons, and their investigations may eventually lead to its application to purposes not yet dreamed of.

During the investigation reported in this paper many ramifications were revealed, in following any one of which a lifetime could be spent. Charcoal, the chief factor, is subject to myriad variations due to differences in raw materials, preliminary treatment, and methods of charring. Added to the variations possible in the charcoal itself are those possible in solutions and in methods of precipitation.

The term "precipitation" as applied to the deposition of gold and silver from cyanide solution on charcoal is a misnomer but it has been so used and will be so used in this paper.

PURPOSE OF INVESTIGATION

The problem of charcoal precipitation of gold and silver from cyanide solution was undertaken by the Rare and Precious Metals station of the Bureau of Mines (Reno, Nev.) primarily to investigate the possibilities in practice and secondarily to investigate the mechanism of the precipitation itself.

The announcement (61, 62) in 1916 that zinc had been displaced as a precipitant by charcoal at the Yuanmi mine, Western Australia,

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again brought the use of charcoal into consideration, and at the suggestion of A. W. Allen, who has made frequent contributions to the literature on the subject, the bureau began the study of the problem. There could be little hope of making a charcoal that would displace zinc, especially as zinc precipitation with the Crowe vacuum method had become practically perfect. It was believed, however, that there might be conditions under which charcoal could be advantageously employed.

SCOPE OF INVESTIGATION

The literature on precipitation from cyanide solution by the use of charcoal is confined almost entirely to studies of the action with gold, and the different theories of the mechanism have been based on the action with gold and not with silver. It was decided, therefore, that the precipitation of both gold and silver should be investigated.

This subject may be studied with respect to increasing the efficiency of charcoal as a precipitant, or with respect to treating it so as to prevent its acting as a precipitant. In the former alternative the object is to produce a charcoal of maximum efficiency and to develop the most favorable conditions for its use; in the latter the object is to prevent "premature precipitation" in the treatment of an ore containing carbonaceous matter.

The investigation included the making of a satisfactory charcoal, and the possible reuse of the charcoal after it had been loaded to its ultimate capacity. Methods of using charcoal and the effect of impurities in solutions were also investigated. Considerable attention was necessarily paid to the theory of precipitation. Incidentally, a method of testing was developed by which comparisons were possible at different stages of the work. The investigation also included a review of the pertinent literature. Appended to this paper is a reference list of articles of particular interest which are referred to by number throughout the text.

RESULTS OF INVESTIGATION

The results obtained in this investigation are summarized as follows:

The mechanism of the precipitation involves adsorption accompanied by a chemical change.

Precipitation of silver on charcoal from cyanide solution follows the same laws as precipitation of gold, although it is slower; charcoal has less capacity for silver than for gold.

The limit of charcoal precipitation from cyanide seems to be about 2,000 ounces of gold and about 1,000 ounces of silver per ton of charcoal.

Little difference exists among charcoals prepared from different woods.

The most important point in the making of charcoal is the heat treatment, either during the making or subsequent thereto.

To quench charcoal does not improve it.

Pulverization finer than 200 mesh does not appreciably add to the efficiency of charcoal.

Few substances in the solution appreciably affect precipitation.

The adsorbed gold or silver salt is soluble to some degree in boiling water, and is especially soluble in hot cyanide.

There is a possibility of so changing the adsorbed gold or silver salt on charcoal that the charcoal may be used for further precipitation.

Charcoal will precipitate gold or silver from a cyanide ore pulp; the charcoal can then be separated from the pulp by flotation.

HISTORY

Metallurgical interest in charcoal as a precipitant has been confined to distinct periods which may be designated as the "chlorination and early cyanide" period, the "premature precipitation" period, and the "Yuanmi" period. Previous to these there was what may be termed the "premetallurgical" period.

Premetallurgical period.—Lowitz (1, 4, 52) in 1790 discovered that charcoal had the power of decolorizing solutions. Early in the nineteenth century several experimenters obtained metallic precipitates on charcoal from solutions (1, 2, 3, 5, 13, 31, 52), and by the middle of the century a considerable amount of empirical knowledge had been published. No distinction was made between adsorption and absorption, although some of the earlier workers seemed to have a shrewd perception of the action of charcoal.

Chlorination and early cyanide period.—The first use of charcoal as a precipitant in metallurgy seems to have been made by W. N. Davis (6, 7, 12, 13) in connection with chlorination. Later it was used in a number of chlorination plants, especially in Australia. Much information has been published on the use of charcoal as a precipitant in the chlorination process (7, 13, 26, 40, 59), but it is now chiefly of historical interest.

As the cyanide process gradually replaced the chlorination process, it was natural that charcoal should be tried as a precipitant for the precious metals from cyanide solutions, especially as the use of zinc was still far from satisfactory. W. D. Johnston (9, 14, 22, 24) in 1894 patented the use of charcoal in pulverized form.

The use of charcoal as a precipitant in the cyanide process became general in Victoria (18, 19, 21, 23, 28, 35, 37, 91), although its use in the United States was confined almost entirely to a few isolated cases of precipitation from waste solutions (43, 91, 93). Little was learned regarding precipitation on charcoal during this period. Observation during practice and a small amount of experiment

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elicited the knowledge that gold was precipitated more rapidly and in greater amounts than silver (23, 28, 37), and that free cyanide had a deleterious effect (14, 35, 38). The charcoal was used in an inefficient manner, and undoubtedly was not very active. As precipitation with zinc shavings improved and became better understood, the use of charcoal and the interest in it gradually declined.

Premature precipitation period.—Interest in charcoal revived when the effect of carbonaceous matter in ores began to be discussed. It resulted in the first definite experimental work, which was done by Morris Green in 1913 (53) and followed shortly by that of W. R. Feldtmann (57). These two investigators materially advanced the knowledge of charcoal precipitation. A great part of the discussion which followed these two papers related purely to theories, many of which were advanced to explain the facts (58, 63, 66). Most of the theories assumed a reduction by some reducing gas in the charcoal (usually assumed to be carbon monoxide), although electrical action, osmotic pressure, and catalysis were not overlooked. Adsorption had been suggested (52, 57, 58, 60), but the action was still regarded as not having been explained (56).

Yuanmi period.—The announcement in 1916 of the use of charcoal as a precipitant in place of zinc at the Yuanmi mine gave a new impetus to discussion and experiment. K. Byron Moore and H. R. Edmands developed and put in practice a method of precipitation on charcoal. They quenched the charcoal while it was red-hot, pulverized it very fine, and passed the solution through three successive charcoal filters (64, 89). The discussion (66, 67, 73, 91) that followed this announcement centered mainly about the effect of quenching and fine pulverizing. It was still believed that carbon monoxide was in some way accountable for the action until A. W. Allen (66), in a contribution to the discussion of Edmands's paper, criticized the different theories, and definitely advanced the theory that adsorption without chemical change of the alkaline aurocyanide was the proper explanation. Allen's conclusions in this and in subsequent articles (67, 93) were generally accepted, as all known facts seemed to bear him out.

Recently (April, 1923), L. B. Williams (98) published further data of experiments made at Yuanmi, showing that the sodium in the ash from the burned charcoal was far from being sufficient to account for the simple adsorption of sodium aurocyanide. The authors of this paper confirm Williams's results, and advance the theory given later in this paper.

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METHOD OF TESTING CHARCOALS FOR PRECIPITATION

The term "activity test," as used in this paper, is a measure of the rate at which charcoal, irrespective of its ultimate capacity, adsorbs gold or silver. The rate is measured by the percentage of metal precipitated.

The term "capacity test" is a measure of the capacity of the charcoal for the gold or silver, or the load that it is able to take, irrespective of the rate at which this load is adsorbed. It is measured in ounces of metal per ton of original weight of charcoal.

The term "per cent efficiency," in the tables, is used as a convenient measure of activity or capacity, 100 per cent efficiency representing either a standard charcoal or a standard condition of test.

NEED OF A STANDARD TEST

In the early part of the investigation the duplication of charcoal precipitation tests with any degree of accuracy proved extremely difficult; two apparently similar tests often varied so as to make comparisons impossible. It was obvious, therefore, that standard conditions of preparing charcoal and a standard method of use must be maintained.

As the amount of charcoal used in a test is important, weighing in the dry state is advisable. Use of wet charcoal is a disadvantage because accuracy of weight is impossible and the water dilutes the solution. Investigation showed that charcoal did not change in weight after wetting and drying at 60° C., so that the dry weight, whether the charcoal was crushed wet or dry, represented the same amount of charcoal.

CONDITIONS AFFECTING TEST

Various conditions that affected the tests were considered and the following were decided to be necessary: (1) Charcoal to be made from the same material; (2) charcoal to be made at a given temperature, with a given time of heating and a definite access of air; (3) charcoal to be pulverized to a determined fineness; (4) charcoal to be fairly freshly made; (5) ratio of charcoal to solution to be a constant; (6) gold or silver content of the solution to be fairly constant; (7) solution to be free from impurities; (8) time of contact between charcoal and solution to be a constant; (9) tests to be made at an approximately constant temperature.

STANDARD TEST

The standard charcoal and the standard conditions adopted were as follows:

Standard charcoal.—Material, pine wood charred in covered crucibles; temperature, 900° C.; time, one-half hour after the inflammable gases ceased coming off; cooled in the covered crucible; pulverized in a porcelain mortar to pass a 200-mesh sieve; weighed dry after drying for several hours at 60° C.

Standard conditions of test.—The standard conditions selected are given in the accompanying table:

Conditions adopted

	Activity tests		Capacity tests	
	Gold	Silver	Gold	Silver
Volume of solution……cubic centimeters	100	100	100	100
$AuKCy_2$ or $AgKCy_2$ to give……milligrams	4	6	15	8
Weight of charcoal……do	200	400	200	300
Time of contact……hours	½	½	48	48
Results figured to	Per cent precipitation.		Ounces of metal per ton of charcoal.	

Agitation	Intermittent but regular.
Temperature	Room.
Solutions to contain	No alkalinity or free cyanide.
Charcoal	Filtered off, washed four times, assayed.
Solutions	Assayed.

NEED OF BOTH ACTIVITY AND CAPACITY TESTS

As the efficiency of a charcoal used as a precipitant for gold and silver from cyanide solution depends upon its activity, or rate of precipitation, and upon its capacity or ultimate load value, these two properties must be measured for correct testing.

Investigations of activated charcoal for adsorbing gas, made during and subsequent to the World War, demonstrated that activity, or rate of adsorption, was not also a measure of capacity. The same was found to be true in the precipitation of gold and silver. Examples are given in Table 1. The figures show that Kelpchar has good activity but low capacity, and that Puffed Rice charcoal has low activity but good capacity.

TABLE 1.—*Capacity and activity comparisons in charcoal*

Charcoal	Activity—precipitation (per cent)	Capacity—load (ounces per ton)
Kelpchar—Au	90.9	209
Kelpchar—Ag	50.5	41
Kelpchar quenched—Au	100.0	682
Kelpchar quenched—Ag	88.8	188
Puffed Rice charcoal—Au	48.0	1,212
Puffed Rice charcoal—Ag	35.4	656
Puffed Rice charcoal quenched—Au	64.7	1,402
Puffed Rice charcoal quenched—Ag	44.8	735

Difference between activity and capacity tests.—A 30-minute contact for activity tests was decided upon. As adsorption is extremely rapid at the beginning, the best measure of activity, or rate, can be obtained by allowing a contact of only a few minutes, provided the contact be stopped immediately and completely; this, however, is not possible because the time of filtration for the different tests of a series may vary. The 30-minute contact gives more accurate comparisons than a shorter period, for the reason that, as the rate is materially slower at the end of the longer period, the percentage of error due to filtration-time variations is decreased.

Forty-eight hours' contact was decided upon for capacity tests, so that equilibrium could be reached; in consequence, more metal was necessary in solution than in activity tests.

In both activity and capacity tests, the amount of gold to charcoal was larger than the amount of silver to charcoal. These ratios were so chosen because charcoal adsorbs silver more slowly and to a much less extent than it adsorbs gold. The important consideration in determining solution strength is to be sure that an excess of metal is present in order to avoid complete precipitation.

MANIPULATION OF TESTS

Capacity tests were made in Erlenmeyer flasks, and activity tests in beakers. With some charcoals, a small amount of charcoal deposited on the glass. When flasks were used they were cleaned out with a rubber-tipped "policeman"; when beakers were used they were cleaned with a small piece of filter paper which was added to the charcoal for assay.

Agitation during tests.—The amount of agitation is not important, especially in long-time tests, though it proved advisable to maintain a certain regularity. With no agitation, activity tests adsorbed 83 per cent as much as with regular agitation, and capacity tests adsorbed 96 per cent as much as with regular agitation.

Temperature during tests.—Temperature, until near the boiling point, does not affect the results of the test; an ordinary variation in room temperature need not be considered.

Filtering charcoal.—As some varieties of filter paper allow finely divided charcoal to pass through, a paper should be selected that does not have this fault.

The charcoal, when filtered, was washed with distilled water four times; the washings were caught with the solution. Although wash water removes a small amount of gold or silver from heavily loaded charcoal, many tests were made in which the solutions, including the wash water, showed no gold or silver, or only a trace, when assayed.

Assaying charcoal.—The charcoal and filter paper were placed in a 10-gram crucible, without cover, ignited at low heat in an electric muffle furnace, and slowly burned to ash. The residue from the ignition was fluxed with a charge consisting of 15 grams soda ash, 5 grams silica, 30 grams litharge, and an excess of flour. The lead button resulting from the fusion was cupeled and the assay was finished in the regular manner.

Assaying solution.—The solution was precipitated with zinc dust and either hydrochloric or sulphuric acid, heated to boiling, and filtered. The filter paper, with the precipitated metal, was placed in a 10-gram crucible, carefully burned, fluxed, fused, and finished in the same manner as the charcoal.

The charcoals and solutions of all tests were always assayed, and the totals were checked against the metal in the original solution. In the accompanying tables the amounts of metal have been omitted for all tests in which solutions of equal metal content were used.

ACTIVITY AND CAPACITY TESTS FOR BOTH GOLD AND SILVER

In order to make true comparisons, it was at first thought necessary to make activity and capacity tests for both gold and silver. Later, on comparing 27 series of tests, it was found that gold and silver activities and gold and silver capacities were fairly comparable; from this discovery it was concluded that silver activity tests are a measure of the gold activity, and that gold capacity tests are a measure of the silver capacity.

The silver activity test was chosen as the measure of activity, because silver, being more slowly adsorbed than gold, does not approach a "clean-up" of the solution so quickly. The gold capacity test was chosen as the measure of capacity, because higher figures for capacity are obtainable with gold, and because the gold assay is more reliable than the silver. Greater accuracy would thus be obtained in the more important test.

COMPARABILITY OF TESTS

A direct comparison of tests made with solutions containing different amounts of gold or silver can not be correctly made, since the precipitation varies with the amount of metal in solution. By plotting the amount of precipitation from solutions containing various amounts of metal, a curve can be prepared by means of which two or more tests can be brought into direct comparison.

SUMMARY

Standard conditions for testing charcoal for precipitation are given. Either silver or gold solutions can be used to measure activity and capacity—silver being used for activity and gold for capacity tests.

MECHANISM OF PRECIPITATION OF GOLD AND SILVER ON CHARCOAL

This paper presents evidence in favor of the theory of adsorption accompanied by a chemical reaction. The differences between ordinary metallic precipitates on charcoal and deposition from cyanide solution will be briefly discussed to show that the gold and silver are not deposited in a metallic condition on the charcoal.

DIFFERENCES BETWEEN METALLIC PRECIPITATES ON CHARCOAL AND DEPOSITION FROM CYANIDE SOLUTIONS

The main differences between metallic precipitates on charcoal and deposition from cyanide solution are as follows: The invisibility of the deposition from cyanide; the chemical difference between the two; the effect of acidity; and the difference on load capacity. Later, evidence of yet another difference will be given—that the deposition from cyanide is an adsorbed salt, and is therefore not in the metallic state.

INVISIBILITY OF DEPOSITION FROM CYANIDE

That metallic gold is visible on charcoal when precipitated from chloride solution, and that metallic silver is visible when precipitated from nitrate solution are facts long known. The deposition from cyanide solution, however, is invisible, a fact noted as to gold by many observers (18, 40, 57, 68), although contradicted by others (24, 45, 53). In the course of this investigation, in no test was there any precipitate seen on any of the many charcoals loaded from gold or silver cyanide, even when the charcoals were examined under the microscope.

CHEMICAL DIFFERENCE OF THE TWO PRECIPITATES

The difference in the solubility of the metallic precipitates from gold chloride or silver nitrate and the gold or silver deposited from cyanide solutions is evidence of chemical difference. It has been noted (44) that gold precipitated on charcoal from chloride solution is soluble in aqua regia, bromine, and chlorine water, and that gold deposited from cyanide solution is not thus soluble (57).

At various times a solvent for gold deposited on charcoal from cyanide solution has been sought. This search has shown (53, 57, 66, 98) that sodium sulphide, potassium hydroxide, and a cyanide solution are solvents.

A reference to the results given in Table 33 shows that solvents of metallic gold or silver are not necessarily solvents for the same metals deposited on charcoal from cyanide solution, whereas many other nonsolvents of the metals do dissolve the precipitates from cyanide solution to a certain extent.

The high dissolving power of sodium sulphide for gold deposited on charcoal from cyanide solution, and its low dissolving power for

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metallic gold precipitated from chloride solution, are shown in Table 31. In these experiments pine charcoal was used, which, after loading, was washed and dried; 250 milligrams of it were agitated 30 minutes with 20 cubic centimeters of the sulphide solution. Sodium sulphide has no effect whatever in dissolving silver from charcoal, whether precipitated from cyanide or nitrate solution.

When the visible metallic precipitate on charcoal is dissolved by a cyanide solution and subsequently deposited in an invisible form, it can well be considered that a different precipitate has been formed (57). In a series of tests a charcoal was loaded with gold from a chloride solution to contain approximately 1,050 ounces per ton; in another series the charcoal was loaded with silver from a nitrate solution to contain approximately 650 ounces per ton. For each test 200 milligrams of the loaded charcoals were added to 50 cubic centimeters of a 2-pound cyanide solution, agitated intermittently for various periods of time, filtered by vacuum, and washed. The results, shown in Figure 1 as smooth curves, indicate that adsorption follows the dissolution of the metallic precipitate so rapidly that part of the change is practically instantaneous, and that some of the dissolved metal never gets outside the pores of the charcoal. As adsorption of silver is less rapid than that of gold, the reaction could naturally be followed better by using charcoal loaded with silver.

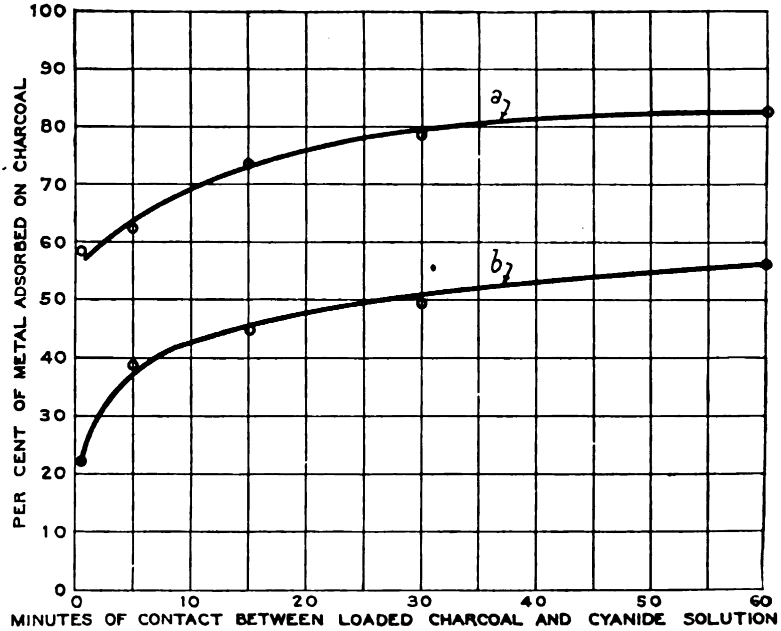

FIGURE 1.—Dissolution of metallic gold and silver from charcoal by cyanide, and their subsequent adsorption: *a*, Gold; *b*, silver

EFFECT OF ACIDITY ON CHARCOAL PRECIPITATION

Table 2 gives the results of several tests which show the retarding effect of acids on metallic precipitation and the increased deposition due to acidification of the cyanide solution, and confirm the results of other investigators (2, 3, 14, 17, 66, 98). Whether or not this increased deposition in acidified cyanide solutions is caused by precipitation of aurous or argentous cyanide, there is at least no evidence that acidifying the cyanide solution retards the precipitation as in the metallic precipitations.

TABLE 2.—*Effect of acidity on the precipitation on charcoal*

Precipitation	Gold		Silver	
	Precipitation (per cent)	Surface tension (dynes)	Precipitation (per cent)	Surface tension (dynes)
Metallic:				
Neutral	97.1	....	99.0	....
½ per cent sulphuric acid	96.9	....	47.1	....
½ per cent nitric acid	93.0	....	73.9	....
½ per cent hydrochloric acid	92.9	....	....	....
Cyanide:				
Neutral	57.4	73.0	52.1	73.0
Sulphuric acid [1]	80.5	73.5	100.0	73.5
Hydrochloric acid [1]	79.6	73.3	100.0	73.5

[1] Solution made barely acid.

DIFFERENCE IN CAPACITY

Many observers (14, 32, 53, 55, 57, 63) have noted an apparent limit to the capacity of charcoal for gold deposited from cyanide solution, although there seems to be no similar limit for metallic precipitation (44). In the Bureau of Mines tests these observations were verified for both gold and silver. A load of 16,700 ounces gold per ton was obtained from a chloride solution, and a load of 3,700 ounces silver per ton from a nitrate solution, both metals being plainly visible as metallic precipitates. From cyanide solutions, the limit of load on pine charcoal was about 2,000 ounces gold and 1,000 ounces silver per ton.

ADSORPTION

A summary of the main characteristics of adsorption (8, 10, 31, 39, 47, 48, 52, 69, 71, 81, 82, 84, 85, 90, 93, 95, 99, 101) from solution follows:

1. Adsorption approaches an equilibrium; that is, in a given solution after equilibrium is reached, a certain amount will have been adsorbed on a given adsorbent, and a certain amount will still remain in solution.
2. Adsorption is very rapid; disadsorption is less rapid than adsorption.

3. Although the effect of temperature is small, adsorption is greater at low temperatures and equilibrium is reached more slowly.

4. Increased pressure gives greater adsorption.

5. The proportion adsorbed from a weak solution is greater than that from a strong solution, although a greater amount is adsorbed from a stronger solution.

6. Adsorption is proportional to the surface of the adsorbent.

7. The present theory of adsorption is that the surface of the adsorbent is covered with a layer of the adsorbed substance not more than one molecule in depth; that is, the layer is monomolecular.

8. There is a maximum adsorption, beyond which increased concentration of solution does not increase the adsorption.

9. Adsorption and the rapidity with which equilibrium is reached depend upon the kind and condition of the adsorbent.

10. Substances that lower the surface tension of the solution tend to adsorb more strongly.

11. Adsorption is proportional to the equivalent or atomic weight of the adsorbed substance.

12. Acids greatly increase the adsorption of anions of neutral salts.

13. An adsorbable substance has the power to replace another adsorbed substance.

14. From a mixture of substances in solution, less of either substance is adsorbed than from a solution of one of the substances.

15. If the ratio of the amount of substance adsorbed, x, to the amount of the adsorbent, m, is plotted against the concentration of the solution at equilibrium, c, the curve is parabolic in the case of true adsorption, and is expressed by the equation $x/m = ac^{\frac{1}{n}}$, in which a and n are constants. By equating the logarithms of both sides, the equation becomes that of a straight line. If, therefore, the logarithms of these two variables (x/m and c) are plotted, a straight line will result if true adsorption has taken place. The straight-line isotherm will not be obtained in adsorption from solutions of strongly dissociated substances and of substances that form hydroxyls.

EQUILIBRIUM POINT

In adsorption the equilibrium point is usually, though not always, reached very rapidly. Tests made with pine charcoal showed that the greater part of the adsorption was rapid and was followed by a lag which probably was due to the time necessary for the solution to enter the less exposed pores. Results of a number of tests indicate that the equilibrium point for gold and silver usually is not reached in 24 hours. This is shown by the results of the tests given in Table 3. In these tests, 250 milligrams of pine charcoal were used with 100 cubic centimeters of gold or silver solution containing 2 pounds of free cyanide and 1 pound of lime per ton.

EFFECT OF TEMPERATURE

The effect of temperature on adsorption from solution is small, although it is generally admitted that increasing the temperature causes a smaller adsorption. Tests made at room temperature and at 80° C. showed that activity was 9 per cent greater and capacity 18.6 per cent smaller with heated solutions.

That a considerably lower capacity would be obtained with heated solutions would be expected because of the solubility of the adsorbed salts in hot water. The activity tests, as they still were far from equilibrium, may not be subject to the solvent action of hot water.

Table 3.—*Loading pine charcoal with gold or silver with varying time of contact*

	Gold—load (ounces per ton)	Silver-load (ounces per ton)
Contact (hours):		
1	729	359
4	840	414
24	1,050	513
48	1,107	565

EFFECT OF PRESSURE

No adsorption tests were made in which increased pressure was used. If increased pressure assists adsorption, a somewhat lower adsorption would be expected when precipitating on charcoal under vacuum—a deduction borne out in the precipitation results given in Table 4.

Table 4.—*Precipitation under vacuum and at atmospheric pressure*

	Under vacuum		Atmospheric pressure	
	Load (ounces per ton)	Precipitation (per cent)	Load (ounces per ton)	Precipitation (per cent)
Gold [1]	793	64.0	888	73.1
Silver [1]	289	30.8	347	39.1
Gold [2]		99.3		98.7
Do.[2]		98.7		99.7
Silver [2]		83.0		90.0
Do.[2]		85.4		91.4

[1] Two hundred and fifty milligrams charcoal, 2 pounds free cyanide; continuous vacuum, charcoal heated red-hot 10 minutes, cooled, added to the solution, and given a 24-hour contact.

[2] Five hundred milligrams charcoal, 2 pounds free cyanide; continuous vacuum, charcoal not heated; contact time, 10 minutes.

ADSORPTION FROM SOLUTIONS OF DIFFERENT STRENGTHS

That a greater percentage but a smaller amount is adsorbed from a weak than from a strong solution is shown clearly by the results of a series of tests given in Table 5. In these tests, 250 milligrams of

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charcoal were given a 24-hour contact with 100 cubic centimeters of a 2-pound cyanide solution containing 1 pound of lime per ton and varying amounts of gold or silver.

TABLE 5.—*Adsorption of gold and silver on charcoal from cyanide with varying values of solution*

Gold					Silver				
Milligrams gold in—			Precipitation (per cent)	Load (ounces per ton)	Milligrams silver in—			Precipitation (per cent)	Load (ounces per ton)
Charcoal	Solution	Total			Charcoal	Solution	Total		
8.86	5.89	14.75	60.1	1,034	3.89	16.77	20.66	18.8	454
9.97	11.37	21.34	46.7	1,163	4.11	21.57	25.68	16.0	479
10.75	16.67	27.42	39.2	1,254	4.65	32.88	37.53	12.4	542
11.30	19.86	31.16	36.3	1,318	4.93	41.19	46.12	10.7	575
11.54	26.00	37.54	30.7	1,346	5.07	46.14	51.21	9.9	591

That adsorption decreases in dilute solutions, even with a constant ratio of metal to charcoal, is shown by Table 6, which gives the results of a series of tests in which the total amount of gold or silver was kept a constant in varying amounts of solution. These solutions were given a 48-hour contact with 250 milligrams of pine charcoal, then filtered and washed.

TABLE 6.—*Adsorption of gold and silver on charcoal from cyanide with varying dilutions*

Volume of solution (c. c.)	Gold					Silver				
	Milligrams gold in—			Precipitation (per cent)	Load (ounces per ton)	Milligrams silver in—			Precipitation (per cent)	Load (ounces per ton)
	Charcoal	Solution	Total			Charcoal	Solution	Total		
50	12.02	12.19	24.21	49.6	1,402	5.99	5.98	11.97	50.	699
100	10.78	13.07	23.85	45.2	1,258	5.87	6.07	11.94	49.2	685
150	10.18	13.46	23.64	43.1	1,188	5.73	6.16	11.89	48.2	668
200	10.07	14.02	24.09	41.8	1,175	5.25	6.58	11.83	44.4	612
250	9.79	14.39	24.18	40.5	1,142	--------	--------	--------	--------	--------

Another proof of decreased adsorption with a more dilute solution was obtained indirectly. Two solutions of gold cyanide were given identical treatment with charcoal for 20 days. One solution, showing 54 per cent precipitation with a load of 842 ounces per ton, was then stopped; the other was diluted with water to five times its original volume and given an additional 6 days of contact, which lowered the precipitation to 46.1 per cent and the load to 705 ounces.

ADSORPTION PROPORTIONAL TO SURFACE

That adsorption is proportional to the surface of the adsorbent is difficult to demonstrate with charcoal because the amount of surface exposed can not be definitely ascertained. However, as more surface is made available for precipitation by pulverizing the charcoal and the precipitating power is thereby increased, this may be considered as a proof that adsorption is proportional to surface.

Pine charcoal has a cellular structure, and the cell partitions have an average thickness of about 0.000005 millimeter. The breaking of these partitions in pulverization gives much less new surface than would result from the pulverization of solids. Pine charcoal has a surface of about 230 square meters per gram; it can be easily shown that the new surface exposed by increased pulverization is extremely small in comparison with the surface already existing.

If the new outer surface obtained by pulverization is assumed to take on a certain load per unit area, the plotting of the results will give a straight line. Plotting the actual increase obtained on charcoal of different mesh, as in Table 24, gives a distinct curve; this indicates that increased adsorption with finer pulverization is due mainly to the opening of pores previously inaccessible to the solution.

MONOMOLECULAR THEORY

When true adsorption takes place, the layer of adsorbed material on the surface of the adsorbent will not be more than one molecule deep. This monomolecular theory was advanced by Langmuir (71), whose experiments on gas adsorption proved that in true adsorption the adsorbed film did not exceed one molecule in thickness.

To determine the amount of gold or silver that charcoal can adsorb if the entire surface be covered with a monomolecular layer, it is necessary that the surface of a given amount of charcoal be known. The figures given by different investigators (76, 81, 83, 86, 100) range from 1,000 square meters per cubic centimeter of charcoal to 131 square meters per gram; this variation is due partly to the different charcoals used, and partly to the fact that the figures are only approximate.

Lowry and Hulett (86) gave the calculated surfaces for four charcoals of different densities, as follows:

Lowry's and Hulett's figures on surface and densities

	Density		Calculated area in square meters	
	True	Apparent	Per gram	Per cubic centimeter
A 909, coconut charcoal (steam activated)	1.84	0.55	230	130
Nela, mixture of coconut charcoals (steam activated)	1.89	.46	440	200
English, birch-wood charcoal (made in gas retort)	1.86	.13	300	40
German, wood charcoal (zinc chloride activated)	1.70	.24	160	40

Pine charcoal was determined by the tests to have a true density of 1.737 and an apparent density of 0.123. This apparent density was that of a piece of charcoal having a volume of 3 cubic centimeters.

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The pores in charcoal differ in size, but with pulverization the larger pores disappear. As the size of charcoal particles diminishes the pore space decreases and the apparent density increases. Apparent density, therefore, is meaningless unless the size of the charcoal particles is known. It is assumed that the surface area of pine charcoal lies between that of the English and German charcoals and measures 230 square meters per gram.

The amount of substance adsorbed upon a surface depends on the molecular weight and the density of the substance. It is assumed that the adsorbed salt was potassium aurocyanide or potassium argentocyanide. The density of these salts was found to be 3.84 and 3.57, respectively.

$M =$ molecular weight of adsorbed substance.

$G =$ density of adsorbed substance.

$\frac{M}{6 \times 10^{23}} =$ weight of one molecule of adsorbed salt, in grams.

$\frac{M}{G \times 6 \times 10^{23}} =$ volume of one molecule of adsorbed salt, in cubic centimeters.

On the assumption that one molecule occupies a surface equal to the square of its diameter, then for 1 gram of pine charcoal the weight in milligrams of a monomolecular layer of adsorbed salt is $26.2\sqrt[3]{MG^2}$; therefore 1 gram of pine charcoal, if the entire surface were covered with a monomolecular layer of adsorbed salt, would contain 442 milligrams of potassium aurocyanide, equivalent to a load of 8,800 ounces of gold per ton of charcoal, or 372 milligrams of potassium argentocyanide, equivalent to a load of 5,880 ounces of silver per ton of charcoal. This is at the ratio of 66.7 per cent silver to 100 per cent gold, which is somewhat higher than was usually obtained. From these figures it appears that, with the maximum loads obtained in charcoal adsorption, only about 23 per cent of the surface is covered in gold precipitation and only about 17 per cent in silver precipitation.

KIND AND CONDITION OF ADSORBENT

That adsorption depends on the kind and condition of the adsorbent seems axiomatic. Differences in adsorption due to these two causes have been noted and commented on (4, 22, 25, 42, 45, 61, 62, 63, 66, 68, 80, 87, 94, 98). In fact, the large amount of work on the activation of charcoals and the production of industrial charcoals (74, 75, 76, 79, 87, 88, 92, 100, 101) is a recognition that the condition of the charcoal is of vital importance to its adsorptive power. The present investigation demonstrated that different kinds of charcoals or carbons differ greatly in precipitating power and that the condition of the charcoal has a remarkable bearing on its action. A reference to the tables—especially Tables 13, 14, 15, 17, 18, 20, 22, 23, 26, 27—shows the difference due to these two causes.

EFFECT OF SURFACE TENSION ON ADSORPTION

The surface tension of the solution has generally been assumed to have an effect on the adsorption of gold from cyanide solution (60, 66, 67, 91). The effect of a change in the surface tension of the solution on the adsorption of gold and silver on charcoal, when this change is brought about by the addition of chemicals, is difficult to determine because chemical action may take place.

An attempt was made to determine whether a change in the surface tension of the solution had any direct bearing on the adsorption of gold or silver salts on charcoal. The surface tension of solvents for the adsorbed salts was noted, as well as the surface tension of solutions in the precipitation of gold and silver.

Surface tension of solutions used in dissolving adsorbed gold or silver salts.—The surface tensions of some of the solutions used in studying the solubility of the adsorbed gold or silver salt were measured. These figures appear in Tables 31, 33, 34, 35, and 37. A study of these results shows that increased dissolving accompanies a decrease in surface tension with ethyl alcohol, ammonium hydroxide, or hot water, and that the reverse is true with potassium cyanide, sodium hydroxide, or sodium sulphide. The results, in general, do not indicate that the dissolving power of solutions depends on a change in surface tension.

Surface tension of solutions in precipitation of gold and silver.—Measurements of surface tensions of some of the solutions used were made to determine the effect of impurities in the solutions. Tables 2, 28, and 29 show that although the added agent may greatly change the activity and capacity of the charcoal, this effect can not be attributed to a change in surface tension, as this is virtually the same for all of the solutions.

ADSORPTION EQUIVALENT TO MOLECULAR OR ATOMIC WEIGHT

That charcoal has greater power to precipitate gold than to precipitate silver from cyanide solutions has been noted (23, 28, 35, 37, 49, 50, 66, 77).

There seems to be a definite relation in the capacity of charcoal for gold and silver adsorbed at equilibrium. If this relation were in direct proportion to the atomic weights of gold and silver the capacity for silver would be 54.7 per cent of that for gold. According to the monomolecular theory, however, the adsorption depends on the specific gravity of the compound adsorbed as well as on the molecular weight; therefore the actual ratio computed on the basis of the adsorption of the alkali aurocyanide or argentocyanide would be 66.7 per cent silver compared to gold. The theoretical ratio is not easily reached when both gold and silver are present in solution.

When, however, two tests are made—one with alkali aurocyanide and one with alkali argentocyanide—if the solutions contain the metals in proportion to the theoretical ratio, and if sufficient time of contact between the solution and the charcoals is allowed for the solution to reach equilibrium, the theoretical ratio is obtained.

EFFECT OF ACIDS IN SOLUTIONS

A number of tests made to compare the adsorptive power of charcoal for gold and silver in acid, neutral, and alkaline cyanide solutions always confirmed the reports that precipitation was greater in acid solutions and less in alkaline solutions (14, 17, 35, 66, 68, 93, 98). Table 2 presents some of the results.

The fact that aurous or argentous cyanide is precipitated upon the acidification of a solution of alkaline aurocyanide or argentocyanide suggests that in acidification some aurous cyanide or argentous cyanide is precipitated, remains with the charcoal when filtered, and is not actually adsorbed. To obtain evidence of this fact the following test was made: A neutral potassium aurocyanide solution was divided into two equal portions; one was left neutral, the other was acidified with sulphuric acid, equivalent to 5 pounds of acid per ton of solution. Each portion was given a 48-hour contact with 0.5 gram of 200-mesh charcoal. The charcoals were filtered off, washed, dried, and 200 milligrams of each were given a 24-hour contact with 20 cubic centimeters of 1 per cent potassium cyanide solution; they were again filtered and washed. In the accompanying table the assays have been converted to a basis of 0.5 gram charcoal for simplicity in comparison.

Comparison of assays of neutral and acid solutions

	Milligrams gold in—			Precipitated or dissolved (per cent)	Load (ounces per ton)
	Charcoal	Solution	Total		
Precipitation from acid solution	47.94	0.03	47.97	99.9	2,796
Precipitation from neutral solution	34.22	13.52	47.74	71.7	1,99
Excess precipitation from acid	13.72				
Extraction from acid-loaded charcoal	27.57	20.37	47.94	42.5	
Extraction from neutral-loaded charcoal	23.45	10.77	34.22	31.5	
Excess dissolved from acid-loaded charcoal		9.60			

Evidently the precipitation from the acid solution was much greater than that from the neutral solution, but 70 per cent of this excess was soluble in the cyanide over and above that naturally disadsorbed. The inference is that a large part or possibly all of the excess precipitation obtained from an acidified cyanide solution is not an adsorbed salt, but is a precipitate of the single cyanide.

When a similar test is made with the alkali argentocyanide, the precipitation of the argentous cyanide takes place at once, and is visible evidence that the precipitation is not all adsorption.

Results demonstrating that hydroxides lower the adsorption of gold and silver, but not until a certain amount is present, appear in Table 30.

A possible explanation of the effect of acids or hydroxides lies in the probability that the gold or silver double salt is ionized, and the negative ions (AuCy or AgCy) are attracted to the positive charcoal in acid solutions but are not attracted to the negative charcoal in alkaline solutions. Several authors (35, 48, 55, 85) have pointed out that acid or alkali solutions cause charcoal to change its sign.

REPLACEABILITY OF TWO ADSORBABLE SUBSTANCES

The monomolecular theory of adsorption leads to the deduction that two adsorbable substances replace each other, and that when present together less of either is adsorbed than when one is present alone. A given surface of adsorbent has a definite capacity for adsorbed molecules; therefore, one substance is adsorbed at the expense of the other substance. Not only is this true when both substances are in solution together, but if subsequently a second substance is given an opportunity to be adsorbed, it actually forces out the first substance by disadsorption. This fact is shown experimentally in the results of the tests given in Table 7. In these tests each solution, consisting of 100 cubic centimeters, was taken from a stock gold solution and a stock silver solution; these stock solutions were neutral and contained no free cyanide. In each test, 200 milligrams of 200-mesh pine charcoal were given a 48-hour contact period, as noted.

The tests indicate that gold equilibrium is represented by a load of 1,221 ounces (as in treatment 1), and silver equilibrium by a load of 588 (as in treatment 3). However, if gold and silver are both present in the solution from the start, the equilibrium is expressed by 1,034 ounces gold and 185 ounces silver (as in treatment 5). These loads show that silver may displace 15.3 per cent of the gold, and that gold may displace 68.5 per cent of the silver. Virtually the same displacement figures are obtained if the silver solution is added (as in treatment 2) after the gold equilibrium has been reached, and also if the gold solution is added (as in treatment 4) after the silver equilibrium has been reached.

TABLE 7.—*Gold displacement by silver and silver displacement by gold*

No.	Treatment	Gold				Silver			
		Milligrams gold in—			Load (ounces per ton)	Milligrams silver in—			Load (ounces per ton)
		Charcoal	Solution	Total		Charcoal	Solution	Total	
1	Au solution only, 48 hours	8.37	2.64	11.01	1,221				
2	Au solution, 48 hours, then added Ag solution, 48 hours	7.35	3.65	11.00	1,070	1.23	4.77	6.00	17
3	Ag solution only, 48 hours					4.05	1.67	5.72	58
4	Ag solution, 48 hours, then added Au solution, 48 hours	6.85	4.12	10.97	999	1.22	4.86	6.08	178
5	Ag solution and Au solution, both at same time, 48 hours	7.09	3.71	10.80	1,034	1.27	4.79	6.06	18

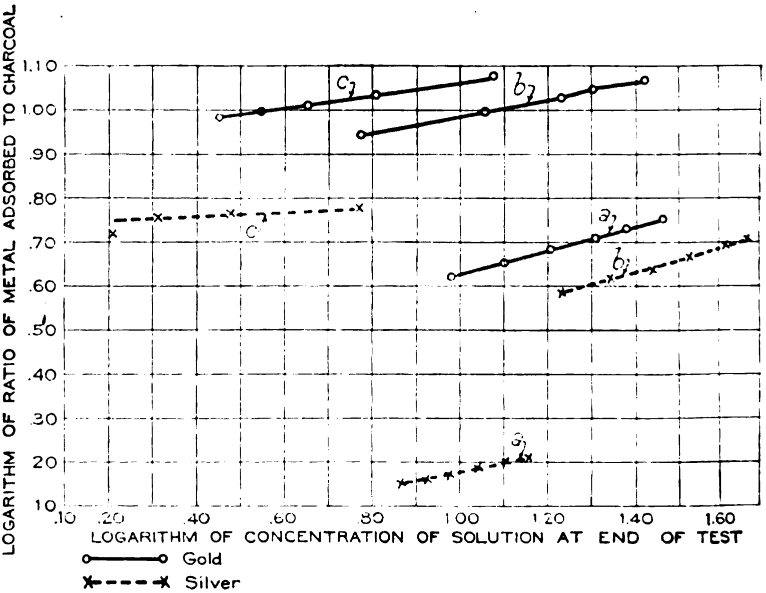

FIGURE 2.—Adsorption of gold and silver on charcoal from cyanide under different conditions: *a*, Varying amounts of charcoal; *b*, varying gold and silver; *c*, varying dilutions

STRAIGHT-LINE ADSORPTION ISOTHERM

Perhaps the best proof of adsorption is the straight-line adsorption isotherm brought out by Freundlich (39). In low-grade solutions where a virtual clean-up of the solution takes place, the straight-line isotherm can not be obtained because at equilibrium the amount of metal left in solution is too small for determination. With solutions containing enough metal in proportion to the charcoal to allow a determinable amount to be left in solution at equilibrium, the adsorption isotherm can be obtained in several different ways.

In this investigation the straight-line isotherm was obtained with different amounts of charcoal, with different solution values, and with different degrees of dilution, as well as by disadsorption with hot water, cyanide solutions, and sodium hydroxide. Characteristic tests and their straight-line isotherms are given herewith for both gold and silver.

Isotherm with varying amounts of charcoal.—In the series with different amounts of charcoal there were six tests for gold and six for silver. Each solution, measuring 100 cubic centimeters, was taken from a stock solution and given a 24-hour contact with pine charcoal; it was then filtered and washed. Table 8 gives the data from which isotherms *a* in Figure 2 were obtained.

TABLE 8.—*Adsorption of gold and silver on charcoal with different amounts of charcoal*

Charcoal (grams)	Gold			Silver		
	Milligrams gold in—			Milligrams silver in—		
	Charcoal	Solution	Total	Charcoal	Solution	Total
0. 125	5. 65	30. 11	35. 76	1. 63	14. 12	15. 75
. 250	10. 87	24. 09	34. 96	3. 19	12. 56	15. 75
. 375	15. 26	20. 28	35. 54	4. 66	11. 06	15. 72
. 500	19. 53	16. 10	35. 63	6. 11	9. 38	15. 49
. 625	22. 43	12. 62	35. 05	7. 28	8. 33	15. 61
. 750	25. 67	9. 70	35. 37	8. 61	7. 27	15. 88

Isotherm with varying solution values.—Table 5 gives the results of a series of tests, five on gold and five on silver, made with a fixed amount of charcoal, but with differing values of solutions; isotherms *b* in Figure 2 were obtained from this series.

Isotherm with varying dilutions.—Table 6 gives the results of a series of tests, five on gold and four on silver, with a fixed amount of charcoal and a fixed total amount of metal in solution, but with different dilutions. These tests gave isotherms *c* in Figure 2.

In all of these isothermal curves the points for gold and silver fall very close to a straight line; the small deviations from the straight line are within experimental error. Only one point for the silver isotherm (*c*) was not well established.

Isotherm from disadsorption.—Efforts to obtain straight-line disadsorption isotherms were fairly satisfactory, especially with gold. As disadsorption depends on the establishing of a new equilibrium, this new equilibrium may be considered as an adsorption equilibrium under new conditions. It is possible that the dissolving of the adsorbed salt by means of a chemical solution may bring in a factor other than simple disadsorption. With hot water, however, the action is probably a simple dissolving effect and, if equilibrium is reached, a straight-line isotherm should result.

A series of charcoals loaded with different amounts of gold or silver were prepared; 1 gram of each was given a 2-hour contact with 80 cubic centimeters of boiling water, and then filtered. The results appear in Table 9, and give the isotherms *a* in Figure 3.

The straight-line isotherm for disadsorption was also obtained by dissolving the adsorbed salts with cyanide. A series of tests with 250 milligrams of loaded charcoal in contact for 2 hours with 20 cubic centimeters of varying strengths of cyanide solution gave the results in Table 9, from which the isotherms *b* in Figure 3 were obtained.

Disadsorption tests were also made by dissolving the adsorbed salts with hot cyanide solutions. In this series, 200 milligrams of loaded charcoal were in contact with 20 cubic centimeters of boiling solution for 1 hour. The results are shown in Table 9, and give the isotherms *c* in Figure 3.

Disadsorption tests were also made by dissolving the adsorbed salts with sodium hydroxide. Four series of tests were made in which 250 milligrams of loaded charcoal were given different periods of contact with 20 cubic centimeters of hydroxide solution. The average of the four tests appears in Table 9, from which the isotherms *d* in Figure 3 were obtained.

TABLE 9.—*Disadsorption of gold and silver from charcoal by means of various agents*

BOILING WATER, VARYING METAL CONTENTS

Gold			Silver		
Milligrams gold in—			Milligrams silver in—		
Charcoal	Solution	Total	Charcoal	Solution	Total
32.00	12.50	44.50	17.37	5.03	22.40
18.17	4.03	22.20	9.22	1.82	11.04
14.64	2.30	16.94	6.94	1.24	8.18
10.40	.78	11.18	3.63	.29	3.92
5.42	.19	5.61			

CYANIDE SOLUTIONS

Solution strength (KCy, per cent)	Gold			Silver		
	Milligrams gold in—			Milligrams silver in—		
	Charcoal	Solution	Total	Charcoal	Solution	Total
1.0	5.30	0.61	5.91	3.10	1.77	4.87
2.0	5.17	.71	5.88	2.40	2.20	4.60
5.0	5.02	.80	5.82	2.20	2.22	4.42
10.0	4.41	1.35	5.76	1.21	3.19	4.40
25.0	4.39	1.49	5.88	.57	4.16	4.73
HOT CYANIDE SOLUTIONS						
1.0	1.80	3.56	5.36	0.36	2.21	2.57
5.0	1.73	3.59	5.32	.32	2.25	2.57
10.0	1.42	3.98	5.40	.17	2.39	2.56
SODIUM HYDROXIDE SOLUTIONS						
[1]10.5	3.70	0.26	3.96	1.665	0.175	1.84
[1]11.0	3.585	.37	3.955	1.625	.225	1.85
[1]15.0	3.40	.595	3.995	1.525	.375	1.90

[1] Solution strength (NaOH, per cent).

All of the disadsorption isotherms, especially those for gold in Figure 3, closely approximate a straight line, and thus show that the adsorption equilibrium of the gold or silver salt adsorbed on charcoal may be reached from either side.

The results obtained by dissolving from charcoal the adsorbed gold or silver salt with different strengths of ethyl alcohol and different strengths of ammonia (Table 34) did not give the straight-line isotherms.

Dissolving the adsorbed gold salt from charcoal by sodium sulphide always gave distinct curves for the disadsorption isotherms. Increased time of contact had no tendency to flatten the curve, possibly because the dissolving of the gold by means of sulphide is not a simple disadsorption.

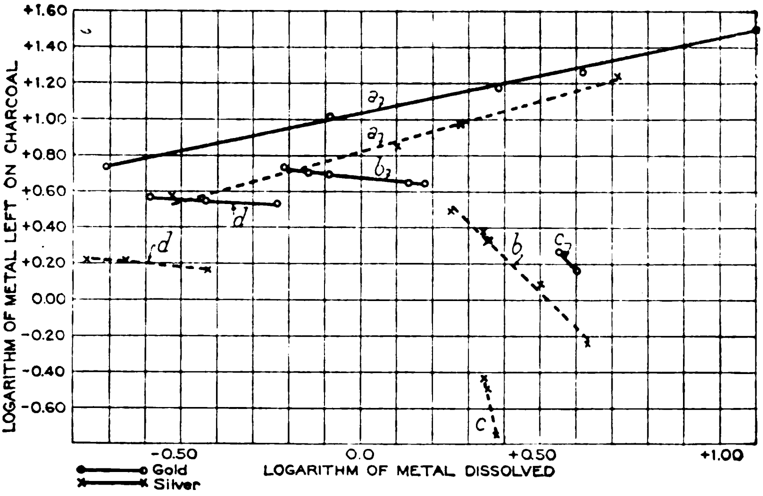

FIGURE 3.—Disadsorption of gold and silver from charcoal with various solvents: *a*, Boiling water as solvent; *b*, cyanide solution as solvent; *c*, hot cyanide solution as solvent; *d*, sodium hydroxide solution as solvent

CHEMICAL ACTION IN CHARCOAL PRECIPITATION FROM CYANIDE

Carbon monoxide theory.—Formerly the chemical theories regarding charcoal precipitation from cyanide solutions required a reducing gas, especially carbon monoxide (16, 22, 32, 40, 42, 51, 53, 57, 58, 61, 63, 66), but more recently, as a result of direct experiment and deduction, observers (66, 67, 70, 77, 91, 93, 98) have generally rejected the idea.

The modern theory of the activation of charcoal, which has been well demonstrated, is that oxidation is necessary at a temperature high enough to decompose and drive off the inactive hydrocarbons that coat the charcoal surface. That charcoal thus activated is a better precipitant than unactivated charcoal is evidence that a reducing gas is not necessary or responsible for the chemical action.

If a chemical change took place during the precipitation, resulting in the formation of either aurous or argentous cyanide, it would be expected that in the decomposition of the double salt, free cyanide or hydroxide would be liberated. However, no free cyanide was detected in the solution after the precipitation of either gold or silver alkaline cyanide, and only occasionally were small amounts of hydroxide detected. These small amounts of hydroxide were attributed to the charcoal itself, as the pine charcoal treated with distilled water gave an alkaline solution.

Simple adsorption of the salt considered.—From the evidence that the mechanism was an adsorption, it was at first thought, in agreement with Allen, that simple adsorption of the gold or silver salt took place without chemical change. There were two reasons for this belief: (1) The color reaction obtained on heating a loaded gold charcoal; (2) the salt extracted with hot water from a charcoal loaded with gold or silver was a double salt.

(1) An alkaline aurocyanide when gradually heated passes through a range of colors—pink, then red, then a deep brownish or purplish red, and finally metallic gold. Pine charcoal loaded from a gold cyanide solution upon gradual heating passes through this identical range of colors—a fact previously noted (68). Aurous cyanide, on the contrary, becomes green when heated, then changes to brown and finally to metallic gold. Unfortunately, the silver salts do not show distinctive colors.

The hot-water extractions from a gold-loaded charcoal, after evaporation and heating, pass through the range of colors obtained by heating the alkaline aurocyanide.

(2) The hot-water extractions give the characteristic precipitates of aurous or argentous cyanides upon acidification with hydrochloric acid, and hydrocyanic acid is liberated. The cyanide is identified in the double salts from this extraction by means of acidification, and also as a product in the precipitation of the metals on aluminum.

The assumption from this evidence that the action is a simple adsorption of the double salt without change naturally implies that if a pure solution of gold or silver double salt were adsorbed on charcoal, the solution remaining would be entirely free from salts if the adsorption were complete and none of the ingredients of the charcoal ash was dissolved. A number of tests were made to verify this assumption. The first tests were with pine charcoal and impure gold and silver salts. In every test, the amount of residue obtained from the solutions was more than could be accounted for by the impurities. As this residue contained no free cyanide and only a negligible amount of hydroxide, the first supposition was that the excess came from the ash in the charcoal, for there was more than enough ash to account for this.

Tests were made with pure salts and with sugar charcoal that had been washed with hot water and dried. This charcoal contained 0.25 per cent ash. In the tests, 5 grams of the charcoal were given a 48-hour contact with 200 cubic centimeters of solution containing in one test 151.20 milligrams $AuKCy_2$ of 96.7 per cent purity, and in the other 110.70 milligrams $AgKCy_2$ of 100 per cent purity. None of the solutions contained free cyanide. A blank charge of 5 grams of charcoal with 200 cubic centimeters of distilled water was also carried through. The solution from the gold precipitation contained 5 milligrams of potassium hydroxide; from the silver precipitation 8 milligrams; and from the blank charge no hydroxide. The solutions were evaporated and the residues weighed. The results, which appear in Table 10, show the solution contained a large excess of residue which could not be attributed to ash in the charcoal. The necessary conclusion was that some chemical action had taken place.

TABLE 10.—*Residue in solution after precipitation on sugar charcoal*

	Gold	Silver
Total residue from solution .... milligrams..	43.61	35.72
Correction, residue obtained from blank charge .... do....	1.67	1.67
	41.94	34.05
Correction due to impurity in salt .... do....	4.99	.00
	36.95	34.05
Correction due to metal not precipitated .... do....	.03	.33
Unaccounted salt left in solution .... do....	36.92	33.72

CHEMICAL ACTION ACCOMPANYING ADSORPTION

Investigation showed that the solution after adsorption consisted almost entirely of a bicarbonate, and that the alkali metal from the alkaline gold or silver cyanide remained in solution. This finding confirmed Williams's observation (98) that the sodium necessary for simple adsorption of $NaAuCy_2$ was not found in the charcoal ash. The evidence was, however, that the adsorbed salt on pine charcoal was a double gold or silver cyanide. A number of analyses of solutions and charcoals finally led to the theory that is herein advanced as a hypothesis of the mechanism of the precipitation, a theory which seems to be in accord with the results obtained.

THEORY OF THE MECHANISM

In the following explanation of this theory, "potassium aurocyanide" is used as a type for any alkaline gold or silver cyanide. The evidence upon which the theory is based is this: A double salt is adsorbed; a bicarbonate solution results; and the potassium remains in the solution.

The first suggestion is that the $KAuCy_2$ is split up into its ions. The negative ion ($AuCy_2$) combines with a positive ion (which must be available in the charcoal) and is adsorbed; the positive ion (K) combines with a negative ion and goes into solution. A natural question is: What compound in the charcoal, upon ionization, can give the results observed? In pine charcoal this could be calcium hydroxide, as 50 per cent of the ash is calcium oxide, and in sugar charcoal the compound apparently can be only water.

The observed differences between gold-loaded pine and sugar charcoals are that the color reaction is not obtained upon heating the sugar charcoal, and that the solubility in hot water of the adsorbed gold salt is different. (It is of interest to note that when sugar charcoal so treated as to contain calcium is used for precipitating gold, the color reaction is observed when the loaded charcoal is heated.)

The solubility by hot water of gold from loaded charcoals varied as follows:

From sugar charcoal, 5.7 per cent; from sugar charcoal partly treated with CaO, 7.9 per cent; from sugar charcoal well treated with CaO, 10.8 per cent; from pine charcoal, 18.1 per cent.

To account for the bicarbonate in the solution it becomes necessary to assume that carbon dioxide is present—a reasonable assumption, since charcoal has a large capacity for this gas (4, 52, 69). The theory may be expressed by the following equations:

For pine charcoal—

$$2\,\mathrm{KAuCy_2} + \mathrm{Ca(OH)_2} + 2\,\mathrm{CO_2} = \mathrm{Ca(AuCy_2)_2} + 2\,\mathrm{KHCO_3}.$$

For sugar charcoal—

$$\mathrm{KAuCy_2} + \mathrm{HOH} + \mathrm{CO_2} = \mathrm{HAuCy_2} + \mathrm{KHCO_3}.$$

The first product of reaction is adsorbed; the second product goes into solution.

Evidence in favor of theory.—In the experiments which led to this theory, it was first conclusively proved that, in the precipitation of $\mathrm{KAuCy_2}$ with pine charcoal, the potassium remained in the solution.

As the evidence indicated that a double salt was adsorbed and the potassium was not adsorbed, calcium, which was present in the charcoal, was suspected of having replaced the potassium. In order to prove this in the adsorption of both gold and silver on pine charcoal, several tests were made in which the charcoals were loaded and washed, then treated with boiling water to dissolve adsorbed salts, and the charcoals and solution were assayed and their calcium content determined. Blank charcoals were carried in parallel to determine the amount of calcium dissolved by the treatment with boiling water alone. The results of these tests showed that: Enough calcium was present in the charcoal to form the calcium double salt; enough calcium was present in the solution from the hot-water extraction to form the calcium double salt; and during precipitation virtually no calcium was removed from the charcoal.

Final tests were made in which charcoal was loaded and then treated with boiling water for two hours. Three products were thus obtained—the charcoal, the solution from precipitation, and the solution from the hot-water extraction. All of these products were analyzed for alkali metal, calcium, and gold or silver. The two solutions (they were free from sulphates, chlorides, and free cyanides) were titrated for hydroxides and bicarbonates, and subjected to evaporation tests.

As only a fraction of the solutions was used in making each of these several determinations, the analytical differences were multiplied; for that reason the obtaining of close quantitative checks could not be expected, although in most of the tests the results were surprisingly close.

Table 11 shows that the alkali metal is not present in sufficient quantity to form the alkaline double salt in the charcoal or in the solution from the hot-water extraction; it remains almost entirely in the solution from precipitation, a small part of it as hydroxide, but most of it as bicarbonate. In the last two tests no calcium was found in the solution from precipitation, but enough was found in the charcoal and in the solution from the hot-water extraction to form the calcium double cyanide.

TABLE 11.—*Analyses of solutions from precipitation and hot-water extractions*

[Weights in milligrams]

	Gold or silver	Na	K	CaO	H_2SO_4 equivalent		Residue by evaporation	Required to form double cyanide			Ratio of metal to CaO
					Hydroxide	Bicarbonate		Na	K	CaO	
Sugar charcoal containing no CaO, using $KAuCy_2$:											
In original material	126.00	------	25.6	------	------	------	------	------	------	------	------
In charcoal after extraction	114.40	------	1.5	------	------	------	------	------	22.6	------	------
In solution from precipitation	2.55	------	21.7	------	4.4	28.4	45.0	------	.5	------	------
In solution from extraction	7.10	------	2.2	------	.0	6.6	10.0	------	1.4	------	------
	124.05	------	25.4	------	------	------	------	------	------	------	------
Per cent dissolved	5.8	------	59.5	------	------	------	------	------	------	------	------
Sugar charcoal, CaO treated, using $KAuCy_2$:											
In original material	125.0	------	25.6	41.8	------	------	------	------	------	------	------
In charcoal after extraction	111.00	------	.4	33.3	------	------	------	------	21.9	15.8	3.00
In solution from precipitation	.35	------	21.0	.0	6.6	24.1	55.0	------	.07	.05	------
In solution from extraction	13.50	------	1.7	5.8	2.2	4.4	37.5	------	2.7	1.9	2.33
	124.85	------	23.1	39.1	------	------	------	------	------	------	------
Per cent dissolved	10.8	------	81.0	13.9	------	------	------	------	------	------	------
Pine charcoal, using $NaAgCy_2$:											
In original material	90.00	19.2	------	------	------	------	------	------	------	------	------
In charcoal after extraction	66.65	1.3	2.6	37.5	------	------	------	14.2	20.3	16.0	1.78
In solution from precipitation	2.95	16.5	7.0	.0	10.9	39.4	85.0	.6	.9	.7	------
In solution from extraction	19.50	2.3	.7	8.3	2.2	8.7	47.5	4.2	6.0	4.7	2.35
	89.10	20.1	10.3	45.8	------	------	------	------	------	------	------
Per cent dissolved	22.6	63.9	21.2	18.1	------	------	------	------	------	------	------

The possible salts in the two solutions of Table 11 have been calculated and are given in Table 12. In this calculation the values for $Ca(OH)_2$ and the AlkOH were based on titration with phenolpthalein. The values for double cyanides were based on gold or silver assays, and the double cyanides were considered to be present as the alkaline salt in the solution from precipitation, and as the calcium salt (when calcium was present) in the solution from the hot-water extraction. The bicarbonates were calculated from the remaining alkali metal; the figures based on titration with methyl orange are given in parentheses. The excess calcium was calculated as carbonate. The last two columns show how closely the total weight of calculated salts compares with the actual weight of the salts obtained as a residue upon evaporation of the solutions.

While the authors recognize that the data at hand do not absolutely prove the presence of these salts in solution, the evidence strongly favors the theory.

TABLE 12.—*Possible salts in solutions from precipitation and from hot-water extraction*

[Weight in milligrams]

	KOH NaOH	$Ca(OH)_2$	$KAuCy_2$ $NaAgCy_2$	$Ca(MCy_2)_2$	$AlkHCO_3$	$CaCO_3$	Total salts	Actual residue
Sugar charcoal containing no CaO, using $KAuCy_2$:								
Solution from precipitation	4.0	----------	3.7	------------	47.2 (57.9)	--------	54.9	45.0
Solution from extraction	.0	----------	10.4	------------	2.1 (13.5)	--------	12.5	10.0
Sugar charcoal CaO treated, using $KAuCy_2$:								
Solution from precipitation	6.0	0.0	.5	0.0	42.8 (49.2)	0.0	49.3	55.0
Solution from extraction	.0	1.7	.0	18.4	4.4 (9.0)	4.6	29.1	37.5
Pine charcoal using $NaAgCy_2$:								
Solution from precipitation	9.9	.0	5.0	.0	58.3 (67.4)	.0	73.2	85.0
Solution from extraction	.0	1.7	.0	32.5	10.2 (14.9)	4.1	48.5	47.5

SUMMARY

The following evidence is given to show that the precipitation on charcoal from cyanide is not metallic: (1) The precipitation is invisible; (2) it has not the chemical properties of the metal; (3) the effect of acidity in solution is not the same as with metallic precipitation; (4) the capacity of charcoal is less than with metallic precipitation.

The mechanism is shown to be an adsorption for these reasons: (1) Equilibrium is established; (2) the action is extremely rapid at first, though a lag, probably caused by inaccessible pores, is noted later; (3) high temperature decreases the capacity of charcoal; (4) lower pressure tends to lower the capacity of charcoal; (5) in strong solutions a large amount of gold or silver is taken up, but in weak solutions a larger percentage is taken up; (6) the amount of metal taken up is greater when more available surface is exposed; (7) the maximum capacity obtained is less than a monomolecular layer of adsorbed salt; (8) activity and capacity differ with different carbons or different conditions of the same carbon or charcoal; (9) the gold and the silver adsorbed are found to replace each other; (10) the straight-line adsorption isotherm can be obtained directly in several ways and indirectly by disadsorption.

A chemical action accompanies the adsorption. The evidence points to a double decomposition; that is, the alkali metal in the alkaline aurocyanide or argentocyanide remains in solution as bicarbonate, and if calcium is available in the charcoal, a double salt, apparently calcium aurocyanide or argentocyanide, is adsorbed.

DIFFERENT CHARCOALS AND THEIR TREATMENT FOR PRECIPITATION

The essential quality of a charcoal for use as a precipitant is high capacity. This might be obtained by: (1) Selection of a suitable raw material; (2) treatment of the raw material before charring; (3) suitable preparation of the charcoal; (4) treatment of the charcoal subsequent to charring, and (5) use of activated industrial charcoals.

Experiments covering these five ways were made. No remarkable charcoal was evolved, but some general conclusions were drawn.

RAW MATERIALS FOR CHARCOAL

A large variety of vegetable and animal substances can yield charcoal or carbon. Several raw materials that might produce charcoals of varying characteristics were tried. These charcoals, and also carbons of different forms, were subjected to the standard tests. The results, given in Table 13, indicate that there is only a small prospect of obtaining a charcoal having a much larger capacity than pine charcoal.

TABLE 13.—*Comparison of carbons and charcoals from different raw materials*

Carbon or charcoal	Activity		Capacity	
	Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
Pine, average of two tests	72.9	100.0	1,499	100.0
Coke, pulverized	2.9	4.0	22	1.5
Coke, quenched	4.4	6.0	26	1.7
Puffed Rice charcoal	35.4	48.6	1,212	80.9
Puffed Rice charcoal, quenched	44.8	61.5	1,402	94.0
Sugar charcoal	47.2	64.8	1,108	73.9
Pine, average of four tests	58.0	100.0	760	100.0
Sugar charcoal	24.1	41.6	637	84.1
Sugar charcoal, quenched	22.8	39.3	626	82.4
Flour charcoal	23.7	40.9	671	88.3
Flour charcoal, quenched	19.6	33.8	675	88.8
Lampblack	5.6	9.7	26	3.4
Lampblack, quenched	8.6	14.8	89	11.7
Coal, carbonized	23.9	41.2	678	89.2
Coal, carbonized, quenched	34.5	59.5	669	88.0
Graphite	2.6	4.5	15	2.0
Graphite, quenched	2.9	5.0	12	1.6

Specimens of 24 different woods were obtained from the Forest Products Laboratory, Madison, Wis. They were charred and the charcoals were tested by standard tests in comparison with pine charcoal. Table 14 gives the results of these tests in comparison with pine. The other woods are listed in the order of their decreasing density. The harder woods generally are near the top of the list.

The results confirm previous observations (22, 23, 28, 55, 62) that softer woods are usually more efficient than harder woods, both for activity and capacity. However, the difference is not large, and the denser woods, if given longer heat treatment during charring, might possibly give as good results (87).[1]

TABLE 14.—*Comparison of charcoals from different woods*

Charcoal	Activity		Capacity	
	Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
Pine (standard)	96.9	100.0	1,871	100.0
Hickory	77.7	80.2	1,525	81.5
Spanish oak	88.4	91.2	1,696	90.6
White oak	82.1	84.7	1,555	83.1
Red oak	84.5	87.2	1,556	83.2
Maple	88.5	91.3	1,668	89.2
Osage orange	86.1	88.9	1,614	86.3
Cherry	89.3	92.2	1,629	87.1
Tupelo gum	88.7	91.5	1,766	94.4
Holly	97.2	100.3	1,865	99.7
River birch	94.9	97.9	1,791	95.7
Elm	89.7	92.6	1,721	92.0
Walnut	89.7	92.6	1,695	90.6
Philippine mahogany	92.4	95.4	1,738	92.9
Ash	90.8	92.7	1,690	90.3
Aspen	93.8	95.8	1,732	92.6
Douglas fir	86.6	89.4	1,639	87.6
Yellow poplar	95.8	98.9	1,820	97.3
Hemlock	93.8	95.8	1,731	92.5
Basswood	91.5	94.4	1,677	89.6
Big tree	86.4	89.2	1,571	84.0
Sitka spruce	94.3	97.3	1,769	94.5
Port Orford cedar	91.1	94.0	1,695	90.6
Cypress	96.0	99.1	1,877	100.3
White pine	95.3	98.3	1,773	94.8

TREATMENT OF RAW MATERIALS PREVIOUS TO CHARRING

Experiments on the treatment of raw materials previous to charring have been reported (33, 85, 92, 100).

In the tests given in Table 15 pine wood was the raw material. Each sample was soaked in the solution for 16 hours before charring, and the tests made under standard conditions. Although several substances increased the efficiency, sodium hydroxide and, in less degree, calcium hydroxide decreased the efficiency.

---

[1] It is of interest to note that, under like conditions of manufacture, both the denser woods and the highly colored woods usually give a much larger yield of charcoal.

TABLE 15.—*Effect of soaking pine wood before charring*

Solution used	Activity		Capacity	
	Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
None, average of two tests	64.3	100.0	990	100.0
1 per cent potassium cyanide	51.2	79.6	1,288	130.1
1 per cent sodium sulphide	98.9	153.8	733	74.0
1 per cent nitric acid	83.2	129.4	1,132	114.3
1 per cent sodium hydroxide	11.2	17.4	437	44.1
1 per cent zinc chloride	72.5	112.8	1,018	102.8
Calcium hydroxide, saturated	45.9	71.4	879	88.8
1 per cent zinc chloride [1]	60.2	93.6	834	84.2
1 per cent zinc chloride [2]	100.0	155.5	891	90.0
1 per cent zinc chloride [3]	99.1	154.1	1,119	113.0
1 per cent zinc chloride [4]	76.2	118.5	1,422	143.6
1 per cent selenium oxychloride	91.6	142.5	1,473	148.8

[1] After charring, treated with 2 per cent sulphuric acid and washed.
[2] After charring, treated with 2 per cent nitric acid and washed.
[3] After charring, treated with 2 per cent hydrochloric acid and washed.
[4] Same as preceding, but reheated and quenched.

METHOD OF PREPARATION OF CHARCOAL

The effects of charring pieces of wood of different sizes, of heat treatment during charring, and of the age of charcoal were investigated. A number of articles discussing in a general way the preparation of charcoals have been published (4, 52, 54, 78, 84, 87, 92, 100, 101).

Size of pieces of wood charred.—Tests were made to ascertain whether charcoal from small pieces of pine differed from that from large pieces. The small pieces were approximately 3/8-inch cubes (as ordinarily used in preparing charcoals for standard tests) and the larger pieces 1½-inch cubes. The heat treatment given was the same for both sizes. In order to ascertain whether the heat treatment was as effective on the inside as on the outside, the charcoal from the larger pieces was divided into two virtually equal portions; one portion composed the outer layer and the other the core. The results of these tests (Table 16) indicate that the size of the pieces from which the charcoal is made has virtually no effect; the inside of the pieces is as efficient as the outside.

TABLE 16.—*Effect of the size at which wood is charred*

Size	Portion	Activity		Capacity	
		Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
3/8-inch, average of 5 tests		46.3	100.0	997	100.0
1½-inch	Outer [1]	40.7	87.9	1,005	100.8
1½-inch	Inner [1]	43.5	93.5	951	95.4
1½-inch	Outer [2]	36.6	79.0	951	95.4
1½-inch	Inner [2]	39.8	86.0	938	94.1
1½-inch	Outer [3]	40.1	86.6	968	97.1
1½-inch	Inner [3]	46.6	100.7	942	94.5
1½-inch, average	Outer	39.1	84.5	975	97.8
1½-inch, average	Inner	43.4	93.7	944	94.7

[1] Quenched, pulverized wet, and dried.
[2] Not quenched, pulverized wet, and dried.
[3] Not quenched, pulverized dry.

Effect of heat treatment on charcoal.—From the argument (20, 22, 40, 52, 55) that reheating a loaded charcoal reactivates it, the deduction can be drawn that heat treatment of charcoal is beneficial. The work of the Chemical Warfare Service demonstrated that heat treatment and oxidation increased the activity of charcoal.

The present investigation of the effect of heat treatment included an examination of the effects of temperature, length of treatment, and broken treatment (heating in two distinct periods). The charcoal was made from ⅜-inch pieces of pine charred over a Bunsen burner in nickel crucibles with ordinary covers. The cover of the crucible fitted just tightly enough to allow gases to escape freely and to allow air to enter. A constant rate of oxidation was maintained; check samples gave the same charcoal yield for equal lengths of time.

The temperature at which charring may be done can vary considerably so long as it is high enough to cause oxidation of the inactive hydrocarbons. The results of the tests (Table 17) show that 500° C. is too low for this oxidation, but 700° C. gives almost as good a charcoal as 900° C. Tests at higher temperature were not made but several authorities (78, 84, 88, 101) assert that activation decreases at temperatures somewhat above 900° C.

TABLE 17.—*Effect of different charring temperatures*

Temperature of charring	Activity		Capacity	
	Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
500° C.[1]	21.3	36.6	382	52.4
500° C.[2]	24.1	41.4	449	61.6
700° C.[1]	56.1	96.4	752	103.2
700° C.[2]	44.1	75.8	717	98.4
900° C.[1]	58.2	100.0	729	100.0
900° C.[2]	51.8	89.0	713	97.8
500° C., 500° C.[3]	17.0	29.2	413	56.7
900° C., 500° C.[3]	56.7	97.4	790	108.4
500° C., 900° C.[3]	60.0	103.1	748	102.6
900° C., 900° C.[3]	65.3	112.2	808	110.9

[1] Charred 10 minutes, not quenched, pulverized dry.
[2] Charred 10 minutes, quenched, pulverized wet, and dried.
[3] Charred 10 minutes at first temperature, cooled, and reheated 10 minutes at last temperature, quenched, pulverized wet, and dried.

It is interesting to note that with equal heat treatments at 900° C., irrespective of other conditions, the results are similar. A temperature of 900° C. was used as standard for charring in three series of tests to determine the effect of time. The results of these tests (Table 18) show that increased duration of heat treatment gives increased efficiency up to a certain point, beyond which there seems to be no gain. The results also show that so long as the total period of heat treatment is the same, applying the heat in two periods

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instead of one does not affect the efficiency of the charcoal. Figure 4 shows that too short a period of heat treatment gives a decidedly inferior charcoal, but prolonging the treatment beyond a certain point confers no benefit.

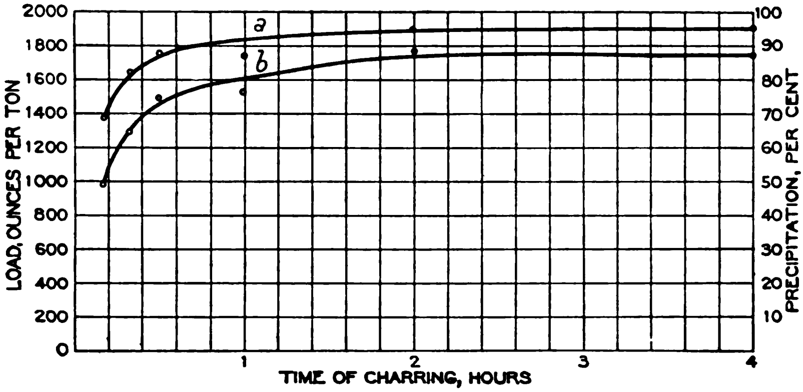

FIGURE 4.—Charcoal efficiency with varying time of charring, all at 900 C.: *a*, Capacity; *b*, activity

TABLE 18.—*Effect of time in the heat treatment of charcoal*

Average minutes heated	Number of tests	Activity		Capacity	
		Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
10[1]	2	64.3	100.0	990	100.0
10[2]	2	74.3	115.5	1,449	146.4
10[3]	2	82.6	128.5	1,617	162.3
10[4]	------	74.1	100.0	1,805	100.0
30	------	71.4	96.4	1,797	99.6
30[3]	------	89.4	120.7	1,989	110.2
60	------	90.6	122.3	2,004	111.0
10	2	49.6	100.0	1,369	100.0
20	2	65.2	131.5	1,642	119.9
30	2	75.0	151.2	1,772	129.4
60	2	76.2	153.7	1,751	127.9
120	2	89.6	180.6	1,913	139.7
240	2	88.2	177.8	1,926	140.7

[1] Cooled and reheated 5 minutes.
[2] Cooled and reheated 15 minutes.
[3] Cooled and reheated 30 minutes.
[4] Cooled and reheated 20 minutes.

Effect of age on charcoal.—The general belief has been that charcoal must be freshly burned to be efficient (32, 51, 53); only one reference (25) giving the contrary opinion has been noted.

Results of a series of tests of pine charcoal of various ages appear in Table 19. They show that a charcoal once activated for precipitation purposes seems to retain its power with very little diminution. The charcoals were made under standard conditions of heat treatment and were kept in the laboratory in beakers with watch-glass covers. They were pulverized dry to minus 200 mesh just before the tests were made. The results show that the activity of the charcoal slowly decreased with age, but the capacity was undiminished during storage for at least one month.

TABLE 19.—*Efficiency of pine charcoal at various ages*

Age of charcoal in days	Activity		Capacity	
	Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
Newly made	81.4	100.0	1,639	100.0
1	86.6	106.4	1,708	104.2
3	81.4	100.0	1,670	101.9
5	79.1	97.2	1,665	101.6
8	80.8	99.3	1,708	104.2
14	77.9	95.7	1,699	103.7
36	76.5	94.0	1,697	103.5
49	76.1	93.5	1,692	103.2
61	66.7	81.9	1,565	95.5

TREATMENT OF CHARCOAL SUBSEQUENT TO CHARRING

Under the heading "Treatment of charcoal subsequent to charring" are given results obtained by steaming, by quenching, by pulverizing, and by chemical treatment.

Certain tests (see Tables 17 and 18) in which the charcoal received a heat treatment after charring can be properly included under this head, but it was deemed best to consider the subject of heat treatment separately.

Steaming charcoal.—Steaming charcoal at high temperature has been found to activate it greatly for gas adsorption (33, 74, 75, 76, 79, 87, 92, 101); the authors tried this method on pine charcoal. They put lump charcoal in a porcelain tube and heated it in an electric furnace, passing steam through the tube until the charcoal cooled enough to avoid ignition. The results (Table 20) show that steaming pine charcoal at the higher temperatures increases its efficiency somewhat, especially as to its capacity for the 5-minute period. From these results, however, it would seem that if a charcoal has been properly heat treated, steaming can not greatly improve it for precipitating gold and silver from cyanide solution.

TABLE 20.—*Effect of steaming pine charcoal*

Steaming		Activity		Capacity	
Temperature, °C.	Time (hours)	Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
No steaming, average of two tests [1]		73.5	100.0	1,144	100.0
620	1 [1]	80.5	109.5	1,139	99.6
620	2 [1]	87.2	118.7	1,147	100.3
620	4 [1]	88.8	120.8	1,152	100.7
620	6 [1]	87.5	119.0	1,097	95.9
750	1 [1]	93.6	127.3	1,225	107.1
750	2 [1]	96.1	130.8	1,207	105.5
750	4 [1]	93.2	126.8	1,087	95.0
750	6 [1]	93.7	127.5	1,185	103.6
900	½ [1]	93.7	127.5	1,252	109.4
900	1 [1]	95.4	129.8	1,358	118.7
No steaming [2]	([1])	91.0	123.8	1,288	112.6
900 [3]	5 minutes	82.2	111.8	1,544	135.0
900 [4]	5 minutes	77.0	104.8	1,496	130.8
900 [5]	5 minutes	88.2	120.0	1,711	149.6

[1] Five-tenths gram of charcoal used in activity tests and 0.25 gram in capacity tests
[2] Charcoal was wet, heated to 900° C., cooled, and pulverized dry.
[3] Cooled after steaming and pulverized dry.
[4] Cooled after steaming and pulverized wet.
[5] Quenched after steaming and pulverized wet.

The formation of water gas is so rapid during steaming at high temperature that pine charcoal is completely consumed in one hour.

Effect of quenching charcoal.—Articles and discussions on the effect of quenching charcoal (61, 62, 63, 66, 67, 77, 93, 98) have been numerous. Edmands (66) concluded that quenching, followed by wet pulverizing, materially increased the precipitating efficiency of charcoal. Since the tests in Table 21 do not confirm this, it is suggested that Edmands's quenched charcoal was superior because it had received a better heat treatment.

In this investigation, before the effect of heating was realized, beneficial effects had always been obtained from quenching, and it was concluded that quenching itself was beneficial. Upon an examination of the data, it became evident that charcoal efficiency was always increased when the charcoal had been given longer heating.

Quenching in water.—The results of a number of tests (Table 21) show that quenching did not materially affect the charcoal efficiency. Although certain individual cases showed a difference, the average of all the tests was so nearly the same that it seemed fair to conclude that no beneficial results could be obtained by quenching.

TABLE 21.—*Comparison of nonquenched with quenched charcoal*

Charcoal	Nonquenched		Quenched	
	Precipitation (per cent)	Load (ounces per ton)	Precipitation (per cent)	Load (ounces per ton)
Pine, pulverized dry	48.0	1,053	41.5	1,022
Pine, outer portion	36.6	951	40.7	1,005
Pine, inner portion	39.8	938	43.5	951
Pine, charred at 500° C	21.3	382	24.1	449
Pine, charred at 700° C	56.1	752	44.1	717
Pine, charred at 900° C	58.2	729	51.8	713
Pine, steamed at 900° C	82.2	1,544	88.2	1,711
Sugar charcoal	24.1	637	22.8	626
Flour charcoal	23.7	671	19.6	675
Coal, carbonized	23.9	678	34.5	669
Burrell, 50-minute	83.6	1,571	86.3	1,660
Pine, charred 10 minutes	50.4	1,374	48.7	1,363
Pine, charred 20 minutes	63.1	1,651	67.5	1,633
Pine, charred 30 minutes	82.9	1,871	66.6	1,673
Pine, charred 1 hour	79.4	1,817	73.0	1,684
Pine, charred 2 hours	88.8	1,900	90.3	1,925
Pine, charred 4 hours	89.2	1,937	87.2	1,916
Average	55.96	1,203.3	54.73	1,199.5

If quenching a red-hot charcoal is the cause of its increased efficiency, equally good charcoals should be obtained by quenching at a certain temperature, irrespective of the duration of the heating. Table 22 gives the results obtained with charcoals made from the same pine but given varying lengths of heat treatment at 900° C. before quenching. The results of the first six tests show that although all charcoals were quenched from 900° C. their efficiency varied with the length of the heat treatment. The results of the last four tests show that two charcoals given 30 minutes total heat treatment are virtually of equal efficiency, as are two charcoals given a 1-hour heat treatment. The latter charcoals were the more efficient, although all were quenched from 900° C.

TABLE 22.—*Effect of heat treatment on pine charcoal before quenching*

Heat treatment at 900° C. (minutes)		Activity, precipitation (per cent)	Capacity, load (ounces per ton)
5		65.0	968
15		73.8	1,433
30		80.0	1,617
5		63.7	1,012
15		74.8	1,496
30		85.2	1,617
Charring at 900° C. (minutes)	Reheating at 900° C. (minutes)		
10	20	74.1	1,805
30		71.4	1,797
30	30	89.4	1,989
60		90.6	2,004

Quenching may be advantageous in washing out impurities and thus lowering the ash contents, or by having a mechanical effect, making a dense charcoal more porous. Quenching reduced the ash content of pine charcoal, especially when the heat treatment had been long.

Quenching in a chemical solution.—Table 23 gives the results of quenching charcoal in chemical solutions. After quenching and pulverizing, the charcoals were washed. In the table comparison is made with the same charcoals quenched in water. The results show that quenching in certain chemical solutions has an effect. Solutions of nitric acid, zinc chloride, and sodium hydroxide, which increased the activation of the charcoal, are of especial interest. Other solutions may have a more decided effect (68).

TABLE 23.—*Effect of quenching charcoal in chemical solutions*

Charcoal	Chemical solution used	Activity—precipitation (per cent)	Capacity—load (ounces per ton)
Pine	Water	52.1	1,002
Do	Hot water	47.5	1,094
Do	1 per cent KCy	44.8	1,119
Do	1 per cent Na_2S	58.5	904
Do	1 per cent HNO_3	100.0	961
Do	1 per cent NaOH	71.4	1,095
Do	1 per cent $ZnCl_2$	81.8	1,130
Do	Saturated $Ca(OH)_2$	55.1	922
Coal, carbonized	Water	34.5	669
Do	5 per cent HNO_3	51.2	685

Effect of pulverizing charcoal.—The effect obtained by pulverizing charcoal may depend on the fineness of pulverization or on the method of pulverization.

Fineness of pulverization.—That fine pulverization increases adsorption has been often recognized and much discussed (9, 52, 61, 62, 63, 64, 66, 67, 73, 80, 92, 93, 98).

Ordinary sieve sizing gives a series of sizes; the coarser sizes may be harder charcoal of a different kind from the finer sizes. To obviate this possibility, the authors of this paper pulverized and sieved the charcoal in such a manner that each size represented the original sample. Table 24 gives the results of a series of standard tests of various sizes of pine charcoal thus obtained; from them the curves given in Figure 5 were obtained. A study of these curves leads to the conclusion that fine pulverization after reaching 200 mesh does not materially increase the efficiency of pine charcoal. At this size all the pores seem accessible enough to take a full load, although this load is taken up somewhat more slowly than in the finer sizes. Investigators (83, 86) have noted that the fine grinding of charcoal does not materially increase the surface available for adsorption.

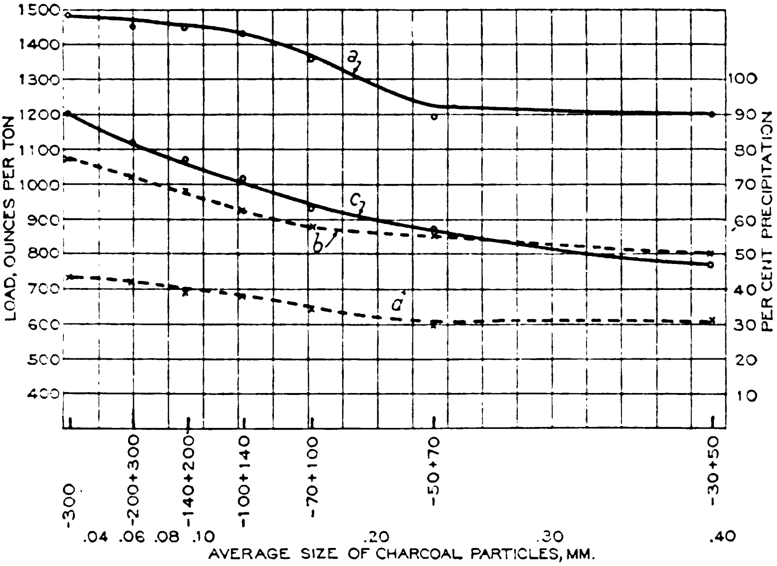

FIGURE 5.—Precipitation of gold and silver on charcoal of different sizes: *a*, Gold capacity; *b*, silver activity; *c*, gold activity; *d*, silver capacity

TABLE 24.—*Precipitation of gold and silver on charcoals of different mesh*

Mesh of charcoal	Activity				Capacity			
	Gold		Silver		Gold		Silver	
	Precipitation (per cent)	Efficiency (per cent)	Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
− 30+ 50	46.4	52.1	49.5	64.8	1,196	81.2	607	83.7
− 50+ 70	56.9	63.9	55.2	72.3	1,190	80.8	591	81.5
− 70+100	62.5	70.2	57.8	75.7	1,353	91.9	642	88.9
−100+140	70.3	79.0	61.6	80.6	1,425	96.1	677	93.4
−140+200	76.3	85.7	66.9	87.6	1,435	97.4	681	93.9
−200+300	81.5	92.0	71.5	93.6	1,444	98.0	713	98.3
−300	89.0	100.0	76.4	100.0	1,473	100.0	725	100.0
−300 [1]	71.2	80.0	48.6	63.6	681	46.2	322	44.4
−300 [2]	79.5	89.3	55.9	73.2	837	56.8	372	51.3

[1] Pulverized dry 19 hours.

[2] Pulverized wet 19 hours.

The precipitation on the interior surface of charcoal can be demonstrated by loading a fairly large grain and then slowly heating it. If just after the metal forms on the surface the charcoal is allowed to cool and is broken open, the interior part will be black and show no metal; but when the charcoal is again heated the newly exposed surface shows metal. After the complete burning of a heavily loaded charcoal a skeleton of metal remains.

In view of the possibility of surface being increased, charcoal pulverized extremely fine was tried. The results are also given in Table 24. One lot of the minus 300-mesh charcoal was pulverized wet, the pulp being just wet enough to flow, for 19 hours in a laboratory pebble mill, and another lot pulverized dry in the pebble mill for 19 hours. The minus 300-mesh charcoal contained 2.2 per cent ash, but after pulverization wet it contained 43.2 per cent and after pulverization dry it contained 16.2 per cent ash, the increase being derived from the pebbles or the jar. Allowance was made for this ash so that the actual amount of charcoal used was the same in all tests.

Instead of the efficiency being increased by the very fine pulverizing it decreased surprisingly. The excessive ash present was not the apparent cause of this decrease, as the wet pulverized charcoal had more ash than the dry pulverized and gave better results. The authors suggest that the long period of pulverizing with an excessive weight of pebbles so changed the surface of the charcoal that it lost some of its adsorptive power.

Excessively fine pulverization, apart from the diminished precipitating power, has two disadvantages—greater difficulty in filtering, and the larger ash content due to long pulverizing in the pebble mill.

Manner of pulverization.—The use of wet pulverization to increase the precipitating efficiency of a charcoal has been widely discussed

(61, 62, 63, 66, 93, 98). A number of tests were made to compare the efficiency of wet and dry pulverized charcoals, the only factor varied being the manner of pulverizing. The results of these tests (Table 25) fail to substantiate the claim that wet pulverizing is beneficial. It may be that in former comparisons of wet and dry pulverizing, the wet pulverized charcoal had been quenched, thus bringing in the additional factor of heating before quenching.

Another question is whether charcoal is better pulverized in a pebble than in a ball mill. Table 25 shows that pine charcoal may be pulverized dry or wet, in iron or porcelain, with equally good results.

TABLE 25.—*Comparative activity and capacity tests for dry and wet pulverized charcoals*

Charcoal	Dry pulverized		Wet pulverized	
	Precipitation (per cent)	Load (ounces per ton)	Precipitation (per cent)	Load (ounces per ton)
Pine, not quenched	48.0	1,053	50.0	952
Pine, quenched	41.5	1,022	46.7	1,002
Pine, outside portion	40.1	968	36.6	951
Pine, inside portion	46.6	942	39.8	938
Pine, steamed at 900° C. 5 minutes	82.2	1,544	77.0	1,496
Pine, pulverized in porcelain	55.2	690	56.2	700
Pine, pulverized in iron	55.5	703	53.7	680
Burrell 50-minute, unquenched	56.6	1,530	58.4	1,533
Burrell 50-minute, quenched	86.3	1,660	92.5	1,702
70-minute Absorbite, unquenched	58.1	1,495	66.3	1,553
70-minute Absorbite, quenched	94.1	1,695	94.5	1,674
Average	60.4	1,209	61.1	1,198

Chemical treatment of charcoal.—Interesting results (11, 12, 15, 30, 57, 92, 97, 101) have been obtained as to the effect of chemical treatment of charcoal. Most of the results, however, refer to gas adsorption.

Table 26 gives results obtained by the chemical treatment of charcoal subsequent to charring. Zinc chloride, nitric acid, and selenium oxychloride treatments seem to give promise of increasing the efficiency, whereas potassium cyanide, sodium sulphide, sodium hydroxide, calcium hydroxide, and sulphuric acid decrease the efficiency, although subsequent heating and quenching restore the original efficiency.

TABLE 26.—*Effect of chemical treatment on charcoal subsequent to charring*

Substance used in treatment	Activity		Capacity	
	Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
None, average of 6 tests	61.5	100.0	945	100.0
CO gas [1]	82.7	134.5	785	83.1
H gas [1]	58.8	95.6	720	76.2
KCy, average of 2 tests [2]	64.7	105.2	857	90.7
KCy [3]	22.9	37.2	599	63.4
Do.[4]	32.5	52.8	640	67.7
Na_2S, average of 2 tests [2]	53.8	87.5	932	98.6
Na_2S [3]	21.6	35.1	548	58.0
Do.[4]	40.8	66.3	569	60.2
HNO_3, average of 2 tests [2]	76.0	123.6	1,113	117.8
HNO_3,[3]	100.0	162.6	682	72.2
Do.[4]	15.9	25.9	541	57.2
NaOH, average of 2 tests [2]	60.4	98.2	843	89.2
NaOH [3]	40.0	65.0	588	62.2
Do.[4]	50.1	81.5	627	66.4
$Ca(OH)_2$, average of 2 tests [5, 2]	56.9	92.5	881	93.2
$Ca(OH)_2$ [5, 3]	29.0	47.2	665	70.4
Do.[5, 4]	29.9	48.6	666	70.5
$ZnCl_2$, average of 2 tests [2]	95.3	155.0	1,022	108.2
$ZnCl_2$ [3]	78.8	128.1	697	73.8
Do. [4]	70.5	114.6	675	71.4
Do. [6]	100.0	162.6	1,158	122.5
Do. [7]	92.9	151.1	1,181	125.0
H_2SO_4 [8]	36.5	59.3	658	69.6
HCl [8]	73.6	119.7	703	74.4
$SeOCl_2$, 5 per cent [9]	100.0	162.6	2,029	109.1
$SeOCl_2$, 10 per cent [9]	100.0	162.6	2,036	109.6
$SeOCl_2$, 100 per cent [9]	100.0	162.6	2,106	113.4
$SeOCl_2$, 5 per cent [10]	100.0	162.6	1,460	78.5
$SeOCl_2$, 10 per cent [10]	100.0	162.6	2,078	111.9
$SeOCl_2$, 100 per cent [10]	100.0	162.6	2,062	111.0
$SeOCl_2$, 10 per cent [11]	100.0	162.6	1,843	99.2

[1] Passed through the charcoal in the cold one-half hour; pulverized dry.

[2] Pine charcoal in small lumps soaked 16 hours in 1 per cent solution, then heated, quenched, and pulverized.

[3] Pine charcoal in small lumps soaked 16 hours in 1 per cent solution, then dried, and pulverized dry.

[4] Pine charcoal in small lumps soaked 16 hours in 1 per cent solution, then pulverized wet.

[5] Saturated solution.

[6] Pine charcoal in small lumps soaked 16 hours in 1 per cent solution, then heated 15 minutes at 900° C., cooled and treated with 2 per cent HCl solution.

[7] Same as (6), but, after the HCl treatment, was reheated and quenched.

[8] Soaked 15 minutes in 5 per cent solution, and washed.

[9] Pine charcoal soaked 1 hour, washed, dried, and pulverized dry.

[10] Pine charcoal soaked 2 hours, washed, dried, and pulverized dry.

[11] Pine charcoal soaked 1 hour in hot solution, washed, dried, and pulverized dry.

A charcoal given proper heat treatment equals any of the chemically treated charcoals. Certain results obtained in the activity tests (in which a complete clean-up of the solution resulted) suggest the possibility of obtaining a charcoal with a greater capacity for silver.

Activated industrial charcoals.—During the war the activation of charcoal for gas masks was very successful. The following activated industrial charcoals were tested for precipitation of gold and silver from cyanide:

Burrell 40-minute and Burrell 50-minute, Burrell Technical Supply Co., Pittsburgh, Pa.

145A—30-minute Absorbite, 155A—40-minute Absorbite, 156A—50-minute Absorbite, 157A—55-minute Absorbite, 70-minute Absorbite, Barnebey Cheney Engineering Co., Columbus, Ohio.

The seven foregoing charcoals had bright, hard, dense grains, finer than six-mesh.

Barnebey-Cheney No. 1, Barnebey Cheney Engineering Co., Columbus, Ohio.

Super-Filtchar, Industrial Chemical Co., Tyrone, Pa.

The two foregoing charcoals had soft, dull grains, finer than six mesh, mostly very fine.

Barnebey-Cheney No. 2, Barnebey Cheney Engineering Co., Columbus, Ohio; this charcoal had bright, hard, dense grains, finer than 12-mesh.

Suchar was a light, fluffy, and very fine material.

Kelpchar was a light, rather fine material produced from kelp.

Table 27 compares the results with those obtained in tests of pine charcoal that had been quenched and pulverized wet. The reader will note that the efficiency of the coarse grains was very low for both activity and capacity, undoubtedly because the pores were too small for efficient precipitation of gold and silver from cyanide solutions. When pulverized, these charcoals compare favorably with pine charcoal, and their efficiency is improved by heating and quenching. None of the results, however, was any better than those later obtained with pine charcoal that had received a sufficient heat treatment.

TABLE 27.—*Industrial charcoals compared to pine charcoal*

Charcoal	Activity		Capacity	
	Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
Pine	48.7	100.0	1,363	100.0
Burrell 40-minute [1]	3.1	6.4	814	59.7
Do.[2]	57.0	117.0	1,317	96.6
Do.[3]	99.3	203.9	1,715	125.8
Burrell 50-minute [1]	9.0	18.5	999	73.3
Do.[2]	41.5	85.2	1,308	96.0
Do.[3]	89.2	183.2	1,748	128.2
Barneby C. 145A [1]	28.6	58.7	579	42.5
Do.[2]	48.1	98.8	1,126	82.6
Do.[3]	99.1	203.5	2,080	152.6
Barneby C. 155A [1]	31.6	64.9	799	58.6
Do.[2]	47.7	97.9	1,254	92.0
Do.[3]	88.1	180.9	1,590	116.7
Barnebey C. 156A [1]	29.8	61.2	774	56.8
Do.[2]	37.1	76.2	955	70.1
Do.[3]	88.4	181.5	1,722	126.3
Barnebey C. 157A [1]	4.7	9.6	798	58.5
Do.[2]	54.3	111.5	1,356	99.5
Do.[3]	91.1	187.1	1,802	132.2
70-minute Absorbite [1]	10.4	21.3	840	61.6
Do.[2]	62.5	128.3	1,348	98.9
Do.[3]	96.1	197.3	1,559	114.4
Barnebey C. No. 1 [1]	23.6	48.5	1,048	76.9
Do.[2]	48.2	99.0	960	70.4
Do.[3]	49.1	100.8	1,248	91.6
Super-Filtchar [1]	21.0	43.1	1,226	90.0
Do.[2]	61.1	125.5	1,356	99.5
Do.[3]	82.3	169.0	1,646	120.8
Barnebey C. No. 2 [4]	7.5	15.4	753	55.2
Do.[2]	24.6	50.5	1,158	85.0
Do.[3]	88.7	182.1	1,791	131.4
Suchar [5]	59.0	121.1	644	47.3
Do.[6]	82.3	169.0	1,053	77.3
Kelpchar [5]	15.3	31.4	261	19.2
Do.[6]	39.5	81.1	853	62.6

[1] Coarse portion only, over 16 mesh, not pulverized.

[2] Pulverized dry to pass 200-mesh sieve.

[3] Quenched and pulverized wet to pass 200-mesh sieve.

[4] Coarse portion only, over 20 mesh, not pulverized.

[5] As received.

[6] Quenched only; not pulverized further.

SUMMARY

Wood is a suitable raw material for making charcoal and, though the difference in the woods tested was small, the softer woods are somewhat better.

Preliminary treatment of the wood before charring does not give promising results; hydroxides are actually detrimental.

The size of the pieces of wood charred has no effect on the efficiency of the charcoal.

The most important detail in making charcoal is heat treatment accompanied by oxidation either with steam or air. The efficiency depends on the total time of the heat treatment given during or subsequent to charring.

Age (to one month) does not diminish the efficiency of pine charcoal.

The evidence indicates that quenching does not increase the efficiency of charcoal; the apparent activation of the charcoal by quenching may be traced to heating before quenching. Quenching in certain chemical solutions has a good effect.

The pores of pine charcoal at 200 mesh are readily accessible to the solution; finer pulverizing is of little benefit, and excessively fine grinding is detrimental.

Dry pulverization is as effective as wet pulverization.

The chemical treatment of charcoal seemed of promise in a few tests only.

Industrial charcoals, if pulverized, are good precipitants, but they are not superior to well-made pine charcoal.

EFFECT OF SUBSTANCES IN SOLUTION ON PRECIPITATION

An investigation was made of the effects of substances found in the ordinary solutions used in cyanide mills, especially free cyanide and hydroxides.

EFFECT OF VARIOUS SUBSTANCES

In one series of tests with pine charcoal the solution contained 1 pound of free cyanide and 1 pound of substance per ton. The results, arranged according to decreasing capacity, appear in Table 28; they show that usually an added agent somewhat decreases the efficiency of the charcoal although few seriously affect the capacity. Usually activity is good when capacity is good, but the opposite holds for iodine. The substances that are most effective in lowering the capacity of the charcoal for precipitation are generally also good solvents for the adsorbed salt—a natural result, since the solvent power counteracts the precipitating power (57, 66, 84, 93).

TABLE 28.—*Effect of various substances in solution*

Agent added	Activity			Capacity		
	Precipitation (per cent)	Efficiency (per cent)	Surface tension	Load (ounces per ton)	Efficiency (per cent)	Surface tension (degrees per square centimeter)
Antimony chloride [1]	73.4	116.9	----------	1,336	119.7	----------
Potassium arsenate	71.1	113.2	----------	1,321	118.4	----------
Rotten wood [2]	56.5	90.0	----------	1,251	112.1	----------
Potassium ferricyanide	95.1	151.4	73.1	1,174	105.2	73.1
Sodium persulphate	98.2	156.4	73.1	1,171	104.9	73.2
Zinc chloride	87.1	138.7	----------	1,142	102.3	----------
Copper sulphate	65.5	104.3	73.2	1,117	100.1	73.2
None, average of three tests	62.8	100.0	----------	1,116	100.0	73.0
Ammonium chloride	75.7	120.6	----------	1,091	97.8	----------
Ammonium carbonate	60.3	96.0	----------	1,065	95.4	----------
Ammonium hydroxide	50.8	80.9	----------	1,013	90.8	----------
Air [3]	49.2	78.3	----------	1,008	90.3	----------
Potassium nitrite	52.1	83.0	----------	1,000	89.6	----------
Potassium nitrate	51.2	81.5	----------	992	88.9	----------
Potassium chloride	47.9	76.3	----------	989	88.6	----------
Sodium chloride	45.9	71.7	----------	987	88.5	----------
Potassium ferrocyanide	49.4	78.7	----------	986	88.4	----------
Potassium cyanate	48.4	77.1	----------	980	87.8	----------
Sodium sulphate	46.6	74.2	----------	978	87.6	----------
Potassium sulphocyanate	47.3	75.3	----------	968	86.7	----------
Suspended clay	51.2	81.5	----------	958	85.8	----------
Sodium carbonate	42.3	67.4	73.1	958	85.8	73.1
Sodium silicate	50.3	80.1	----------	946	84.8	----------
Cupric chloride	51.3	81.7	----------	935	83.8	----------
Potassium carbonate	44.3	70.5	----------	935	83.8	----------
Sodium peroxide	41.6	66.2	----------	922	82.6	----------
Pine wood [4]	36.1	57.5	----------	856	76.7	----------
Potassium zincate	38.0	60.5	----------	821	73.6	----------
Bleach powder	52.3	83.3	73.1	700	62.7	73.1
Tannic acid	29.9	47.6	73.1	677	60.7	73.1
Iodine	88.8	141.4	73.1	411	36.8	73.1

[1] Only partly dissolved.
[2] Soaked in solution one-half hour.
[3] Passed through solution during entire test.
[4] Soaked in solution 2½ hours.

EFFECT OF SODIUM SULPHIDE

In Table 29 sodium sulphide, an excellent solvent for the gold salt, is shown to decrease gold precipitation. The effect of the sulphide on silver precipitation can not be studied easily, owing to the precipitation of silver sulphide.

TABLE 29.—*Effect of sodium sulphide in solution on the precipitation of gold*

Sodium sulphide (pounds per ton solution)	Activity		Capacity		
	Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)	Surface tension (degrees per square centimeter)
None	52.1	100.0	1,002	100.0	73.0
1	5.4	10.4	414	41.3	----------
5	2.9	5.6	73	7.3	----------
10	2.0	3.8	34	3.4	73.7

EFFECT OF FREE CYANIDE AND ALKALIES

That a solution containing free cyanide lowers the precipitation on charcoal, and that hydroxides have a depressing effect, are facts that have been noted (14, 35, 48, 57, 66, 67, 98).

From the fact that free cyanide and hydroxides are good solvents of the adsorbed gold and silver salts, one would expect that they would also have a depressing effect on the adsorption. The effect of these agents was studied in a series of tests in which both the free cyanide and the alkalinity were varied. The results, given in Table 30 and graphically shown in Figure 6, indicate that very low alkalinity has a beneficial effect, and that the depressing effect does not begin until the alkalinity passes 0.5 pound per ton. It is also evident that sodium hydroxide is more detrimental than calcium hydroxide.

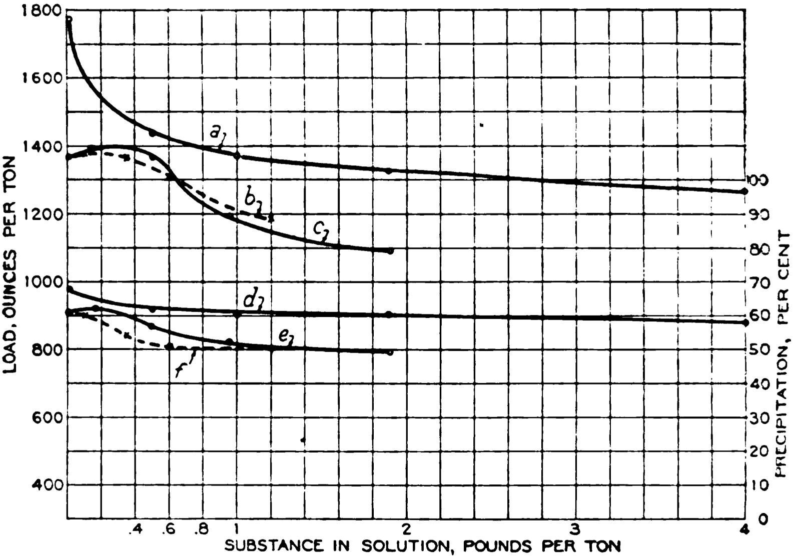

FIGURE 6.—Effect on precipitation by cyanide, calcium hydroxide, and sodium hydroxide: *a*, Cyanide capacity; *b*, NaOH capacity; *c*, $Ca(OH)_2$ capacity; *d*, cyanide activity; *e*, $Ca(OH)_2$ capacity; *f*, NaOH activity

TABLE 30.—*Effect of free cyanide and alkalinity in solution*

Pounds in solution			Activity		Capacity	
KCy	$Ca(OH)_2$	NaOH	Precipitation (per cent)	Efficiency (per cent)	Load (ounces per ton)	Efficiency (per cent)
--------	--------	--------	68.4	100.0	1,766	100.0
0.50	--------	--------	61.7	90.2	1,435	81.3
1.00	--------	--------	60.2	88.0	1,365	77.3
1.95	--------	--------	59.8	87.4	1,337	75.7
4.00	--------	--------	57.6	84.2	1,267	71.7
1.00	--------	--------	60.2	88.0	1,365	77.3
1.00	0.15	--------	61.2	89.5	1,382	78.3
1.00	.55	--------	56.5	82.6	1,362	77.1
1.00	.95	--------	51.5	75.3	1,187	67.2
1.00	1.90	--------	49.1	71.8	1,082	61.3
1.00	--------	--------	60.2	88.0	1,365	77.3
1.00	--------	0.10	59.6	87.1	1,374	77.8
1.00	--------	.35	53.9	78.8	1,353	76.6
1.00	--------	.60	50.8	74.3	1,312	74.3
1.00	--------	1.20	50.0	73.1	1,186	67.2
--------	.50	--------	57.0	83.3	1,549	87.7
.45	.50	--------	56.7	82.9	1,380	78.1
1.65	.50	--------	54.3	79.4	1,254	71.0
3.35	.50	--------	53.5	78.2	1,270	71.9

SUMMARY

Few substances in solution have a bad effect on the precipitation of gold or silver on charcoal.

Sodium sulphide in solution decreases the precipitation of gold.

Free cyanide in solution decreases the precipitation of both gold and silver.

Hydroxides in solution, when present in amounts less than 0.5 pound per ton, increase the precipitation of both gold and silver, but when present in greater amounts decrease it.

REMOVAL OF ADSORBED GOLD AND SILVER SALTS FROM CHARCOAL

Tests on the removal of the adsorbed gold or silver salt from charcoal were made by amalgamation, by dissolving the adsorbed salt, and by electrolysis.

AMALGAMATION

Tests made to remove gold by amalgamation confirm the conclusion (18) that the gold in the ash from charcoal which has been used for the precipitation of gold from cyanide solution will not amalgamate.

A loaded charcoal was thoroughly washed, dried, heated to a red heat in a covered crucible for five minutes, and quenched. It was then ground wet in a porcelain mortar with mercury, but only a trace of gold was amalgamated. Reheating the same charcoal for an additional period of 15 minutes and then grinding again with mercury gave the same result. Finally the charcoal was burned to an ash in which metallic gold was plainly visible; the ash was ground wet in a mortar with mercury, but the gold entirely failed to amalgamate.

Sodium amalgam, ground wet for 20 minutes with a gold or silver loaded charcoal, removed about 10 per cent of the metals, but the results indicated that the sodium hydroxide formed during the tests had a solvent action on the gold and silver salts, as most of the dissolved metal was found in solution.

SODIUM SULPHIDE AS A SOLVENT FOR ADSORBED GOLD SALT

Since a number of tests have shown sodium sulphide solution removes practically none of the adsorbed silver salt from charcoal, only its solvent power for the gold salt will be considered here.

The results of a number of tests in which 250 milligrams of loaded pine charcoal were given various periods of contact under varying conditions with 20 cubic centimeters of solution are given in Table 31. The results show that strength of solution has a greater effect than length of contact, whereas heating the solution does not increase its solvent power (except slightly with a weak solution), and does actually decrease it.

TABLE 31.—*Solvent power of sodium sulphide for gold on charcoal*

Strength of solution (per cent Na_2S)	Surface tension (dynes)	Contact (minutes)	Condition of test	Per cent dissolved after—	
				Adsorption from cyanide solution	Precipitation from chloride solution
0.1		5	Cold	57.7	
.5	73.3	5	do	72.0	
1.0	73.8	5	do	77.3	
2.0	74.3	5	do	81.5	
.1		10	do	62.1	5.0
.5		10	do	73.7	3.4
1.0		10	do	80.5	2.6
2.0		10	do	85.2	2.6
.1		30	do	63.1	.9
.5		30	do	79.0	2.6
.5		30	Hot	90.9	
1.0		30	Cold	83.5	1.8
1.0		30	Hot	72.6	
2.0		30	Cold	88.2	1.8
2.0		30	Hot	42.4	
5.0		30	Cold	93.1	
5.0		30	Hot	74.9	
.1		60	Cold	57.0	
.5		60	do	75.2	
1.0		60	do	83.8	
2.0		60	do	89.1	

A test was made to study the effect of successive sulphide treatments with intermediate precipitations. A liter of a 2-pound cyanide solution was prepared, containing approximately 0.30 ounce of gold per ton and 2 pounds of protective alkalinity per ton. One gram of pine charcoal was added to 400 cubic centimeters of the stock solution and given a 30-minute contact. The charcoal, after filtering and washing, was added to 10 cubic centimeters of 5 per cent sodium sulphide solution, given a 30-minute contact, and then filtered and washed. The charcoal was again used to precipitate 200 cubic centimeters of the solution, and then subjected to a sulphide treatment as before. The cycle was repeated until there were four precipitations and four sulphide treatments. The charcoal, each solution from precipitation, and each solution from the sulphide treatments were assayed. The results in Table 32 show that precipitation in each case was good, undoubtedly because the charcoal capacity had not been reached; but the successive sulphide solutions dissolved constantly decreasing amounts, indicating that the charcoal would rapidly reach the limit of capacity and the point where no more dissolving would take place.

TABLE 32.—*Decreasing solvent power of sodium sulphide for gold with successive treatments*

	Milligrams gold in—			Newly precipitated gold (milligrams)	Gold precipitated (per cent)	Gold dissolved at each operation based on—	
	Charcoal	Solution	Total			Total gold in charcoal (per cent)	Newly precipitated Au (per cent)
First precipitation	4.15	0.03	4.18	4.15	99.3		
First dissolving	.53	3.62	4.15			87.2	87.2
Second precipitation	2.61	.01	2.09	2.08	99.5		
Second dissolving	.77	1.84	2.61			70.5	88.5
Third precipitation	2.84	.02	2.09	2.07	99.0		
Third dissolving	1.36	1.48	2.84			52.1	71.5
Fourth precipitation	3.38	.06	2.08	2.02	97.1		
Fourth dissolving	2.02	1.36	3.38			40.2	67.3

Even if the gold remaining in the charcoal after a sulphide treatment is insoluble, it is reasonable to expect that the newly precipitated gold would show a constant percentage as soluble. This, however, is not the case, as is shown by the decreasing figures in the last column of Table 32.

Why sulphide dissolves gold that has been adsorbed on charcoal from cyanide solution has been the subject of several discussions (57, 66, 67, 98); practical use has been made of the action in the re-treatment of a graphitic schist after cyanidation (70).

The results of some experiments in which the loss of sodium sulphide when in contact with pine charcoal was determined showed that the amount lost decreased with weaker solutions, but that the percentage lost increased with weaker solutions. This indicated the adsorption of sodium sulphide, although the straight-line adsorption isotherm was not obtained.

VARIOUS SUBSTANCES AS SOLVENTS FOR ADSORBED GOLD AND SILVER SALTS

Table 33 gives results obtained on the solvent powers of various substances for the adsorbed gold and silver salts. In the tests, unless otherwise noted, 250 milligrams of loaded charcoal were given a 1-hour contact with 20 cubic centimeters of 1 per cent solution at room temperature, then filtered, and washed. The results are tabulated according to the diminishing solubility of gold.

TABLE 33.—*Solvent power of various substances for adsorbed gold and silver salts on charcoal*

Solvent	Gold dissolved (per cent)	Silver dissolved (per cent)	Surface tension (dynes per square centimeter) (water, 73 dynes)
Sodium peroxide	27.7	16.8	74.5
Potassium cyanide, 2-hour contact	16.8	32.4	....
Sodium hydroxide	11.9	22.4	....
Potassium hydroxide	6.2	9.5	74.4
Potassium cyanide	5.8	23.8	....
Mercuric cyanide [1]	5.4	8.5	....
Mercuric nitrate [2]	3.1	49.8	....
Bleach powder	2.6	.0	....
Sodium bicarbonate	1.7	6.6	....
Potassium iodide	1.5	3.7	....
Calcium hydroxide, saturated	1.5	.5	....
Mercurous nitrate [2]	1.2	62.8	....
Barium hydroxide, saturated	1.1	.5	....
Sodium carbonate	1.0	4.2	73.6
Ammonium acetate	.9	1.5	....
Sodium nitrate	.8	4.0	....
Ammonium thiocyanate	.8	3.4	....
Sodium pyrophoshate	.8	.0	....
Gold dust soap powder	.8	.0	....
Picric acid, ½ per cent solution	.8	.0	73.1
Potassium ferrocyanide	.6	2.8	....
Mercuric cyanide [3]	.6	.0	....
Potassium nitrite	.5	.0	....
Sodium chloride	.5	.0	....
Bromine [4]	.5	.0	....
Sodium thiosulphate	.4	7.7	73.1
Sodium sulphite	.4	2.2	....
Hydrogen gas [5]	.4	.0	....
Ammonium chloride	.4	.0	....
Ethyl alcohol, 2-hour contact	.3	1.8	....
Aluminum potassium sulphate	.3	.0	....
Potassium bichromate	.3	.0	....
Tannic acid	.2	1.0	73.6
Calcium chloride	.2	.0	73.3
Sodium persulphate	.2	.0	....
Aqua regia	.2	.0	73.3
Potassium ferricyanide	.2	.0	....
Distilled water	.1	1.3	....
Nitric acid	.0	5.4	....
Ferric sulphate	.0	4.1	....
Copper sulphate	.0	3.2	....
Acetic acid	.0	1.4	....
Lead acetate	.0	1.3	....
Ammonium hydroxide, 2-hour contact	.0	1.0	....
Ferrous sulphate	.0	.0	73.4
Bleach powder and sulphuric acid	.0	.0	73.4
Ammonium carbonate	.0	.0	73.5
Pine oil	.0	.0	....
Potassium permanganate	.0	.0	....
Tartaric acid	.0	.0	73.5
Hydrochloric acid	.0	.0	73.2
Sulphuric acid	.0	.0	73.1

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[1] Made by adding NaCy to $HgCl_2$ until precipitate is just dissolved.
[2] Nitric acid added to just short of dissolving.
[3] Made by dissolving Hg_2Cl_2 in NaCy.
[4] Five cubic centimeters saturated solution bromine with 15 cubic centimeters water.
[5] Gas passed through water emulsion.

It is noticeable that the cyanide solutions and alkaline hydroxides head the list for both gold and silver, and that acids are well toward the end. The solvent effect of sodium peroxide can be attributed, in part at least, to its alkalinity, because oxidizers do not seem to have any greater effect than reducers. The outstanding solvent for silver is mercurous nitrate.

The effects of strength of solution, time of contact, and temperature were studied with the most promising solvents.

Effect of strength of solution.—The tests on the effect of the strength of solution in dissolving adsorbed gold and silver salts were made like those reported in Table 33, except where otherwise noted. In general the results (Table 34) show that increased strength caused increased dissolving of the adsorbed salts. With alcohol and ammonia a regular increase with increased strength is evident; with potassium cyanide and sodium hydroxide the increase diminishes with increased strength.

TABLE 34.—*Effect of strength of solution on solvent power for gold and silver*

Solvent	Strength of solution (per cent)	Gold dissolved (per cent)	Silver dissolved (per cent)	Surface tension (dynes per square centimeter)
Sodium carbonate	1	1.0	4.2	----------
	5	1.9	6.2	----------
Acetic acid	1	.0	1.4	68.7
	5	.9	.9	58.9
Potassium cyanide	1	5.8	23.8	75.0
	5	11.3	50.0	77.0
Potassium cyanide (2-hour contact)	1	10.3	36.3	75.0
	2	12.1	47.8	----------
	5	13.7	50.2	77.0
	10	23.4	72.5	----------
	25	25.3	88.0	80.4
Ethyl alcohol	2	.6	1.8	65.2
	25	3.0	4.8	37.9
Ethyl alcohol (2-hour contact)	1	.3	1.8	72.7
	5	.8	1.8	58.8
	10	1.6	----------	----------
	25	1.7	2.0	----------
	50	2.2	3.0	28.3
Ammonium hydroxide (2-hour contact)	1	.0	1.0	----------
	5	5.9	13.5	----------
Ammonium hydroxide	1	.0	1.0	72.9
	2	.3	1.4	----------
	10	1.0	2.1	----------
	25	2.1	4.9	65.4
	50	4.0	10.7	65.2
Mercurous nitrate (5 cubic centimeter solution)	½	.0	25.8	----------
	1	.0	42.8	----------
Sodium hydroxide (½-hour contact)	½	5.3	8.7	73.2
	1	7.4	10.6	73.4
	5	12.8	17.5	76.1
Sodium hydroxide (1-hour contact)	½	6.3	10.2	73.2
	1	8.9	12.3	73.4
	5	14.5	19.9	76.1
Sodium hydroxide (2-hour contact)	½	7.1	9.7	----------
	1	9.8	12.7	76.1
	5	16.1	21.5	----------
Sodium hydroxide (4-hour contact)	½	7.8	9.5	----------
	1	11.3	13.1	76.1
	5	16.1	20.6	----------

Effect of increased time of contact.—The dissolving power of substances for the adsorbed salts increases with the time of contact, although this increase is not great, and there seems to be a limit beyond which no further dissolving takes place. This is particularly noticeable in the silver results, as would be expected if the dissolving action were disadsorption. Some results will be found in Tables 34 and 35.

Effect of temperature.—Since this investigation had shown that hot water had a solvent action on the adsorbed gold and silver salts in charcoal, the effect of hot water was studied, as was also the effect of heating other solvents.

Solubility of adsorbed gold and silver salts in hot water.—Table 35 gives some results of tests of the dissolving effect of hot water under various conditions. In these tests, with the exception of the last five, 250 milligrams of loaded charcoal were used. The table shows that water has little solvent power at temperatures below 60° C. Also, the time of contact and the amount of water used, up to a certain point, has some effect. Especially marked is the increased amount dissolved from more heavily loaded charcoals.

TABLE 35.—*Effect of temperature on solvent power of water for adsorbed gold and silver salts*

Condition of test			Gold		Silver		Surface tension (dynes per square centimeter)
Temperature	Water (cubic centimeters)	Contact (hours)	Total milligrams in test	Dissolved (per cent)	Total milligrams in test	Dissolved (per cent)	
Room	20	1	7.59	0.1	6.82	1.3	73.0
Boiling	5	1	6.71	5.2	2.06	3.9	62.7
Do	20	1	5.85	12.5	4.43	19.5	
Do	100	1	7.46	7.8	6.92	20.5	
Room	20	½	4.44	.0	2.87	1.8	
62° C	20	½	4.43	.4	2.88	2.8	
Boiling	20	½	3.98	10.3	1.87	11.8	
75° C	20	2	5.85	3.2	4.75	4.8	66.7
Boiling	20	2	3.96	14.7	1.82	7.7	
Do	20	4	3.94	17.0	2.03	7.8	
Do	80 to 1 gram charcoal	2	44.50	28.1	22.40	22.5	
			22.20	18.2	11.04	16.5	
			16.94	13.6	8.18	15.2	
			11.18	7.0	5.56	3.8	
			5.61	3.4	3.92	7.4	

As the dissolving power of boiling water decreases rapidly with decreasing loads, it may be assumed that repeated hot-water treatments would not be very effective. This point was verified by a test in which five hot-water treatments were given. Five grams of gold-loaded charcoal were given a one-hour contact with 400 cubic centimeters of boiling water, the water filtered off, and the charcoal given a second treatment with a like amount of boiling water for another hour. This cycle was continued for five successive treatments; then the final charcoal and the five water washes were assayed. Table 36 shows the results.

Table 36.—*Solvent power of hot water for adsorbed gold salt with successive treatments*

Hot-water treatment	Milligrams gold in—			Per cent dissolved	
	Charcoal	Solution	Total	Individual treatment	Cumulative treatment
First	84.41	12.04	96.45	12.5	12.5
Second	81.32	3.09	84.41	3.6	15.7
Third	80.97	.35	81.32	.4	16.0
Fourth	80.91	.06	80.97	.1	16.1
Fifth	80.88	.03	80.91	.04	16.2

Ralston (58) has called attention to the fact that if a solution is used which is capable of dissolving the adsorbed salt, the values would be washed out; but the total removal can be accomplished only with an infinite number of washes. The results of the test do not indicate that this would happen with hot water, as the amount dissolved rapidly approaches zero while a large amount of gold is still in the charcoal.

As hot water has little dissolving effect while its temperature is below boiling, it would be interesting to investigate the effect of boiling water under pressure.

Solubility of adsorbed gold and silver salts in boiling solutions.—Table 37 gives the results of tests with hot solutions of substances that were good solvents at room temperature. In these tests 250 milligrams of loaded charcoal were in contact with 20 cubic centimeters of 1 per cent solution for one hour, unless otherwise noted. The results show that usually the hot solutions dissolve more of the salt than the cold. That heating solutions of mercurous nitrate and nitric acid does not increase their dissolving power for gold is due perhaps to chemical change. The amount of adsorbed salt dissolved by a heated solution is much greater than the sum of that dissolved by a cold solution and by hot water.

Table 37.—*Effect of temperature on the dissolving power of solvents*

Solvent	Temperature	Gold (per cent dissolved)	Silver (per cent dissolved)	Surface tension (dynes per square centimeter)
Mercuric cyanide	Room	0.6	0.0	----------
Do	Boiling	12.5	22.3	----------
Mercurous nitrate	Room	1.2	62.8	73.6
Do	Boiling	1.4	93.7	63.0
Mercurous nitrate, 40 cubic centimeters	do	.5	94.3	63.0
Nitric acid	Room	.0	5.4	73.4
Do	Boiling	.1	88.0	63.8
Sodium hydroxide	½ hour, room	7.4	10.6	73.4
Do	½ hour, boiling	46.3	59.6	63.5
Do	1 hour, room	8.9	12.3	73.4
Do	1 hour, boiling	50.3	64.5	63.5
Do	2 hours, room	9.8	12.7	73.4
Do	2 hours, boiling	50.0	61.6	63.5
Do	4 hours, room	11.3	13.1	73.4
Do	4 hours, boiling	50.7	61.3	63.5
Potassium cyanide, 1 per cent	Room	17.0	32.4	75.0
Do	Boiling	65.7	86.4	64.5
Potassium cyanide, 5 per cent	Room	23.6	52.5	77.0
Do	Boiling	64.8	87.8	66.4
Potassium cyanide, 10 per cent	Room	31.5	66.0	78.0
Do	Boiling	74.4	93.3	69.3

Solubility of adsorbed gold and silver salts in successive hot cyanide solutions.—As there was only a small difference in the dissolving effect with hot cyanide solutions of different strengths, a test was made to determine the result of a succession of low-strength hot cyanide washes. One gram of a gold-loaded and 1 gram of a silver-loaded charcoal were each placed in a filter and wet with water. Ten successive charges of 40 cubic centimeters of 0.1 per cent boiling cyanide solution were passed through each filter, the charcoal being cold at the start; each successive solution was assayed, as well as the final charcoal; no wash waters were used. The results (Table 38) show how the gradual heating of the charcoal affects the rise of extraction in the first four gold solutions. The gold load on the charcoal was reduced from 721 ounces to 69 ounces, and the silver load from 593 ounces to 30 ounces per ton. These results indicate that further treatments would not have greatly increased the gold extraction.

TABLE 38.—*Dissolving adsorbed gold and silver salts from charcoal with successive hot weak cyanide solutions*

Treatment	Gold				Silver			
	Milligrams gold		Per cent dissolved		Milligrams silver		Per cent dissolved	
	In solution	Left in charcoal	Individual treatment	Total	In solution	Left in charcoal	Individual treatment	Total
First	1.00	23.74	4.0	4.0	6.94	13.40	34.1	34.1
Second	1.64	22.10	6.9	10.7	3.64	9.76	27.5	52.0
Third	1.55	20.55	7.0	16.9	2.47	7.29	25.3	64.2
Fourth	2.65	17.90	12.9	27.6	2.16	5.13	29.6	74.8
Fifth	2.31	15.59	12.9	37.0	1.35	3.78	26.3	81.4
Sixth	1.89	13.70	11.5	44.6	.97	2.81	25.7	86.2
Seventh	1.42	12.28	10.4	50.4	.75	2.06	26.7	89.9
Eighth	1.17	11.11	9.5	55.1	.42	1.64	20.4	92.2
Ninth	1.02	10.09	9.2	59.2	.34	1.30	20.6	94.1
Tenth	.86	9.23	8.5	62.7	.27	1.03	20.6	95.4
	15.51				19.31			

ELECTROLYTIC REMOVAL OF ADSORBED SILVER SALT FROM CHARCOAL

Several investigators (29, 36, 41, 46) have worked on the electrolytic removal of gold from charcoal, but no definite results are available.

Table 39 gives the results obtained in a number of tests to recover silver from charcoal electrolytically. Two methods were tried. In one method the loaded charcoal was packed tightly in a porous cell that contained a carbon electrode; in the other method the charcoal was mixed with the electrolyte and allowed to settle onto a carbon electrode. In both tests a platinum cathode was used with a direct current of 7 volts. When the charcoal was simply packed in the porous cell and placed in the electrolyte, no removal of silver salt took place unless the charcoal itself was made the cathode by a reversal of the current previous to the regular operation. The results of these tests are unsatisfactory with respect to electrolytic removal. The results indicate that the electrolyte acted simply as a solvent for the adsorbed silver salt, and that the silver was then deposited electrolytically. This would account for the deposition of silver when the charcoal was not confined in a porous cell, and may also account for the fact that when the charcoal is confined in a porous cell a reversal of the current is necessary before results are obtained. In the sixth test, 20.2 per cent of the silver was deposited when a cell was used without reversal of the current; in this test, as the charcoal was mixed with the electrolyte and then filtered through the porous cell, all the silver deposited was probably in solution before the current was applied. That a sulphuric acid electrolyte proved effective after a preheating of the charcoal may be attributed to the formation, during the heating, of metallic silver, which subsequently dissolved in the acid.

TABLE 39.—*Electrolytic removal of adsorbed silver salt from charcoal*

	Total time of—		Weight of charcoal (grams)	Electrolyte	Distribution of silver—					
					Left in charcoal		Deposited on cathode		Left in electrolyte	
	Reversed current (hours)	Deposition (hours)			Milligrams	Per cent	Milligrams	Per cent	Milligrams	Per cent
Cell	½	2	10	2 per cent NaCy	36.90	86.7	4.68	11.0	0.99	2.3
Do	3	3	10	1 per cent NaCy	143.56	86.6	21.58	13.0	.70	.4
Do	1	1	10	1 per cent NaOH	140.68	98.0	1.23	.9	1.65	1.1
Beaker	None.	6	10	1 per cent NaCy	91.49	65.0	48.49	34.5	.70	.5
Do	None.	5	10	1 per cent NaCy, 1 per cent NaOH	73.49	80.3	17.24	18.9	.76	.8
Cell	None.	2	[1] 10	1 per cent NaCy	58.65	79.8	14.84	20.2	.00	.0
Beaker	None.	1	8	do	30.10	79.7	4.10	10.9	3.56	9.4
Do	1	1	8	1 per cent H_2SO_4	30.10	100.0	.00	.0	.00	.0
Do	None.	2	[1] 8	do	11.60	38.6	9.28	30.8	9.22	30.6
Do	None.	2	8	1 per cent NaCy	8.97	77.3	2.63	22.7	Trace.	.0

[1] The charcoals in these tests were heated to red heat in covered crucibles for 15 minutes and allowed to cool before the test.

SUMMARY

The removal of gold or silver by amalgamation was not successful, either from the adsorbed salts or after their change to the metallic form.

With sodium sulphide, virtually all of the gold, but none of the silver salt, can be removed from a loaded charcoal; stronger solutions and longer contact give better results; heating the solution does not help; its dissolving power decreases rapidly with successive treatments and intermediate precipitations.

Usually a substance that dissolves the adsorbed gold salt also dissolves the adsorbed silver salt; the outstanding exceptions are sodium sulphide which dissolves the gold salt only, and mercurous nitrate which dissolves the silver salt only.

As a rule, hydroxides are more effective than acids in dissolving both the adsorbed salts. There is no marked difference between oxidizers and reducers.

With few exceptions, the dissolving power increases with longer contact, with stronger solutions, and with increased temperature.

Although boiling water is a solvent for the adsorbed gold and silver salts, after the first hot-water treatment only a small part of the remaining salt is soluble in boiling water.

Hot cyanide solutions are effective solvents for the adsorbed gold and silver salts; low-strength solutions are almost equal to stronger solutions in effectiveness. Successive treatments with hot low-strength cyanide solutions give good results.

Attempts to remove electrolytically the adsorbed silver salt from charcoal indicate that the salt must be dissolved in the electrolyte before it can be deposited on the cathode.

LOSS OF CYANIDE IN CHARCOAL PRECIPITATION

That a loss of cyanide occurs when charcoal is used as a precipitant has been generally recognized (14, 18, 22, 23, 27, 28, 34, 38, 66, 72). The average loss noted in 34 precipitation tests was 6.8 milligrams KCy per gram of pine charcoal. The solutions averaged 3.56 pounds KCy per ton before precipitation, and 3.46 pounds after precipitation with 2 hours 26 minutes average contact.

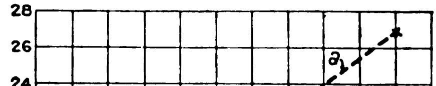

FIGURE 7.—Loss of cyanide in contact with charcoal for varying contact periods and varying strengths: *a*, Varying strengths of solution; *b*, varying contact periods

LOSS DUE TO ADSORPTION

A brief study of the loss of cyanide on charcoal revealed that the loss increased with longer contact and with stronger solutions.

The relation of the loss of cyanide to time of contact and strength of solution is shown in Table 40, which gives the results of a series of tests with 2 grams of pine charcoal and 200 cubic centimeters of solution. To eliminate the natural decomposition of the cyanide, blank charges were carried in parallel throughout. The average cyanide loss for time of contact and strength of solution is plotted in Figure 7.

TABLE 40.—*Loss of cyanide in contact with pine charcoal with varying time of contact and strength of solution*

Time of contact (hours)	KCy (pounds per ton)		KCy loss (pounds per ton)	KCy lost per gram charcoal (milligrams)
	Blank	Test		
1½	1.00	0.90	0.10	5.0
20	1.00	.90	.10	5.0
68	.95	.75	.20	10.0
92	.95	.75	.20	10.0
1½	1.95	1.85	.10	5.0
20	1.95	1.80	.15	7.5
68	1.95	1.60	.35	17.5
92	1.90	1.60	.30	15.0
1½	2.95	2.80	.15	7.5
20	2.90	2.70	.20	10.0
68	2.95	2.55	.40	20.0
92	2.90	2.50	.40	20.0
1½	3.95	3.75	.20	10.0
20	3.90	3.60	.30	15.0
68	3.90	3.50	.40	20.0
92	3.85	3.40	.45	22.5
1½	4.95	4.70	.25	12.5
20	4.90	4.55	.35	17.5
68	4.85	4.40	.45	22.5
92	4.85	4.40	.45	22.5
1½	9.90	9.55	.35	17.5
20	9.80	9.30	.50	25.0
68	9.90	9.30	.60	30.0
92	9.90	9.20	.70	35.0
Average, 1½			0.192	9.6
Average, 20			.267	13.4
Average, 68			.400	20.0
Average, 92			.417	20.9
Average, 1-pound solution			.15	7.5
Average, 2-pound solution			.225	11.2
Average, 3-pound solution			.287	14.4
Average, 4-pound solution			.337	16.8
Average, 5-pound solution			.375	18.7
Average, 10-pound solution			.537	26.8

Table 41 gives the average of four series of tests made with solutions of different strengths. In these tests, 2 grams of pulverized pine charcoal were given 92 hours' contact with 200 cubic centimeters of solution, and blank solutions were carried in parallel. These results show that the actual amounts of cyanide lost increased but the percentage lost decreased with stronger solutions, thus following the adsorption law. Furthermore, by plotting the logarithms of the amounts of cyanide lost against the logarithms of the amounts of cyanide left in solution at the end of the tests, a straight-line isotherm, as given in Figure 8, is obtained.

TABLE 41.—*Loss of cyanide on charcoal with solutions of varying strengths*

Milligrams KCy—			KCy lost or adsorbed (per cent)
In blank at end of test	In solution at end of test	Lost or adsorbed	
79.6	64.5	15.1	19.0
172.4	152.1	20.3	11.8
266.8	242.9	23.9	9.0
392.5	365.1	27.4	7.0
525.1	495.9	29.2	5.6
1,004.2	966.1	38.1	3.8

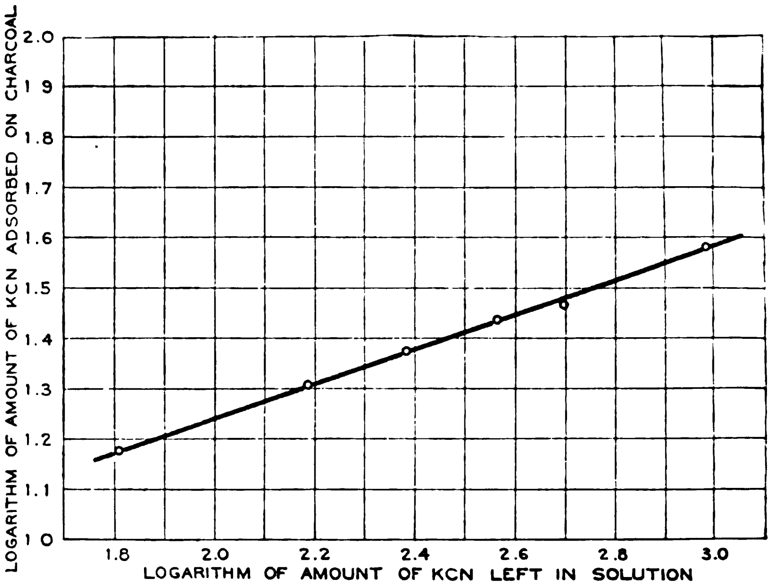

FIGURE 8.—Adsorption isotherm of potassium cyanide on pine charcoal from varying strengths of solutions

REGENERATION OF CYANIDE FROM CHARCOAL

Attempts to remove the adsorbed cyanide from charcoal were not successful, although a number of methods were tried. The results are summarized as follows: (1) The ash from the burned charcoal yielded no free cyanide; (2) fusion of the charcoal with sodium hydroxide or sodium carbonate yielded no free cyanide; (3) complete burning of the charcoal with sodium hydroxide or sodium carbonate yielded no free cyanide; (4) grinding the charcoal with dilute sodium hydroxide yielded no free cyanide; (5) picric acid displaced no free cyanide; (6) treatment of the charcoal with sulphuric acid under vacuum yielded no cyanide; (7) sodium sulphide did not remove free cyanide from the charcoal; (8) sulphureted hydrogen removed 39 per cent of the adsorbed cyanide as thiocyanate, not as free

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cyanide; (9) a boiling solution of 1 per cent sodium hydroxide removed 5.5 per cent of the adsorbed cyanide as free cyanide, and an additional equivalent of 3.7 per cent as other than free cyanide.

A gold-loaded charcoal that contained 15 units of adsorbed cyanide and 65 units combined with gold was treated with sulphuric acid, and heated. No free cyanide was recovered until a large excess of acid was used with continued boiling for 30 minutes under vacuum, and then only 10 units were recovered. No adsorbed cyanide had been recovered in a previous test by this method, a fact which suggests that the cyanide was recovered from the combined cyanide.

Regeneration of cyanide by use of sodium sulphide with charcoal.—In using sodium sulphide under certain conditions with charcoal in the precipitation of silver it was found that free cyanide was regenerated. This result, however, can be traced to the sulphide as a precipitant, and not to the removal of adsorbed cyanide from the charcoal. Apparently there is here very little or no adsorption on the charcoal of free cyanide from the solution. Table 42 gives results of tests in which 1 gram of pine charcoal was used. In the last test when the amount of sulphide used is equal to the theoretical requirement for the precipitation, the regeneration of the cyanide is practically complete, and no cyanide is lost by adsorption.

TABLE 42.—*Free cyanide in solutions when Na_2S was used with charcoal*

Solution for precipitation			Sodium sulphide				Solution after precipitation of KCy (pounds)	
			Solution		Na_2S (milligrams)—			
Cubic centimeters	Silver (milligrams)	KCy (pounds)	Cubic centimeters	Per cent	Necessary to precipitate Ag_2S	Actually used	Actually contained	Should have for complete regeneration
1,000	253	None.	100	0.5	92	500	None.	0.46
1,700	441	0.35	170	.5	160	850	0.35	.82
1,000	250	.35	100	.05	91	50	.30	.80
700	118	.95	8	.5	43	40	1.25	1.26

SUMMARY

The loss of cyanide from a solution in contact with charcoal is evidently due to adsorption.

Attempts to remove adsorbed cyanide from charcoal were not successful.

When sodium sulphide is used as a "fixer," cyanide is regenerated and does not seem to be adsorbed by the charcoal.

PRECIPITATION OF LOW-GRADE AND MILL SOLUTIONS

Although the work done on the precipitation of low-grade and mill solutions was small, the tests made indicate that the precipitation of gold on charcoal can be easily and rapidly obtained from very low-grade solutions. The precipitation of silver from the solutions is slower and the capacity of the charcoal is less.

AGITATION TESTS

Synthetic solutions.—Two liters of solution were prepared, containing 0.30 milligram of gold as $AuKCy_2$ (equivalent to 9 cents per ton), with no free cyanide or alkalinity. This solution was given a 1-hour contact with 5 grams of 100-mesh pine charcoal (5 pounds of charcoal per ton of solution).

One liter of solution was prepared, containing 3.16 milligrams of silver as $AgKCy_2$ (equivalent to 0.09 ounce per ton), with no free cyanide or alkalinity. This solution was given a 1-hour contact with 5 grams of 100-mesh pine charcoal (10 pounds of charcoal per ton of solution).

In both tests all the tail solution was assayed; the results appear as test A in Table 43. Although this precipitation is complete, the amount of charcoal used was large and the time of contact was long.

TABLE 43.—*Precipitation of a low-grade solution with charcoal*

Test	Contact (minutes)	Charcoal (pounds per ton solution)	Milligrams metal in—			Load on charcoal (ounces per ton)	Precipitation (per cent)
			Charcoal	Solution	Total		
A. Gold	60	5	0.30	Trace.	0.30	1.8	100.0
A. Silver	60	10	3.16	Trace.	3.16	18.5	100.0
B. Gold	5	1	.36	Trace.	.36	10.5	100.0
B. Silver	7	2	2.08	0.83	2.91	60.7	71.5

Therefore two tests were made in which the charcoal and time of contact were materially reduced. Two liters of gold solution containing 0.36 milligram of gold (equivalent to 10½ cents per ton), with no free cyanide or alkalinity, and 1 liter of silver solution containing 2.91 milligrams of silver (equivalent to 0.086 ounce per ton), with no free cyanide or alkalinity, were used. One gram of 100-mesh pine charcoal (1 pound of charcoal per ton of solution for the gold and 2 pounds per ton for the silver) was used in each solution. In both tests the charcoal and the solution were mixed and then filtered at once; the maximum time of contact given with the gold solution was five minutes, and with the silver solution seven minutes. The results (test B in Table 43) show that the precipitation of gold was rapid and the precipitation of silver was much slower.

Mill solutions.—Two liters of a mill solution that assayed 0.11 ounce of silver and 0.0013 ounce of gold per ton, and contained 0.013 pound KCy and 0.004 pound protective alkalinity per ton, were agitated with 1 gram of 100-mesh pine charcoal for 1 minute; another 2 liters were agitated for 10 minutes, and then both were filtered. The maximum time of contact was 10 minutes and 30 minutes, respectively. The results (Table 44) show the benefit of longer contact with the charcoal. The precipitation of silver is so slow that longer contact, more charcoal, or a countercurrent precipitation is necessary.

Further tests showed the same results. Although the precipitation of gold was very rapid and complete, the precipitation of silver was not satisfactory unless the contact between the charcoal and the solution was prolonged.

Table 44.—*Precipitation of a low-graae mill solution with charcoal*

	Time (minutes)		Milligrams metal in—			Load on charcoal (ounces per ton)	Precipitation (per cent)
	Agitation	Maximum contact	Charcoal	Solution	Total		
Gold	1	10	0.09	Trace.	0.09	2.6	100.0
Silver			2.56	4.63	7.19	74.7	35.6
Gold	10	30	.09	Trace.	.09	2.6	100.0
Silver			3.33	3.58	6.91	97.1	48.2

THREE-STAGE PRECIPITATION

The difficulty in obtaining good precipitation of silver from low-grade solutions suggested three-stage precipitation, in which the ongoing solution first meets a partly loaded charcoal and finally passes through a fresh charcoal. This is, in effect, a countercurrent method (61, 62, 63, 64, 66, 89). Stage precipitation is not new, as most charcoal precipitation methods were of this nature (9, 17, 19, 21, 23, 28, 37).

Three tubes, 2.6 centimeters in diameter and 10 centimeters long, were fitted up as filters. The three filters were placed one above another; the solution that passed through one filter was received by the next, and finally left the last filter as tail solution.

Two grams of 100-mesh pine charcoal were fed wet to each filter, forming a filter bed one-half inch deep. The charcoals used in the first two filters were given a preliminary loading with solution identical with that of the test.

A mill solution was used, assaying 3.32 ounces silver, 0.04 ounce gold, and containing 0.40 pound KCy and 0.12 pound of protective alkalinity per ton. For the preliminary loading, the first charcoal was given a half-hour contact with 120 cubic centimeters diluted to 300 cubic centimeters, and the second was given the same contact with 30 cubic centimeters diluted to 300 cubic centimeters. This preliminary loading gave 12.55 milligrams silver, equal to a load of 183 ounces per ton, and 0.16 milligram gold, equal to a load of 2.3 ounces per ton, for the first charcoal; and 3.34 milligrams silver, equal to a load of 49 ounces per ton, and 0.03 milligram gold, equal to a load of 0.4 ounce per ton, for the second charcoal.

The original mill solution was diluted with tap water, so that it contained 0.33 ounce of silver, 0.004 ounce of gold, and 0.04 pound KCy, and 0.01 pound P. A. per ton, and 2,400 cubic centimeters of this diluted solution were passed through the three filters by gravity filtration. The rate of filtration gradually slowed down and was periodically renewed by gently stirring the top of the charcoal bed. The average rate was 0.24 cubic centimeter per minute, giving an approximate contact period of five minutes in each filter. At this rate 2.98 square feet of filter area are required in each filter to precipitate 1 ton of solution in 24 hours. Each charcoal and the entire tail solution were assayed. The results (Table 45) show that practically all the precipitation took place in the first two filters, and suggest that filtration could be faster or that more solution could be put through the filters.

Table 45.—*Three-stage precipitation of low-grade mill solution with charcoal*

	Original loading		Total loading		Loading due to test		Precipitation (per cent)
	Milligrams	Ounces per ton	Milligrams	Ounces per ton	Milligrams	Ounces per ton	
Silver:							
First charcoal	12.55	183	27.86	406	15.31	223	60.6
Second charcoal	3.34	49	13.10	191	9.76	142	38.6
Third charcoal	.0	.0	.21	3	.21	3	.8
Tail solution					Trace.		
Total					25.28		100
Gold:							
First charcoal	.16	2.3	.42	6.1	.26	3.8	100
Second charcoal	.03	.4	.03	.4	.0	.0	.0
Third charcoal	.0	.0	.0	.0	.0	.0	.0
Tail solution					.0		
Total					.26		100

To test more rapid filtration, the three filters were connected with a vacuum, and the preceding test was duplicated in all other particulars. The preliminary loading gave 12.38 milligrams silver, equal to a load of 180 ounces per ton, and 0.16 milligram gold, equal to a load of 2.3 ounces per ton, for the first charcoal; and 3.34 milligrams silver, equal to a load of 49 ounces per ton, and 0.04 milligram gold, equal to a load of 0.6 ounce per ton, for the second charcoal.

The rate of filtration maintained was 0.65 centimeter per minute, or a contact period of two minutes in each filter. At this rate 1.13 square feet of filter area would be required in each filter to precipitate 1 ton of solution per 24 hours. The results (Table 46) show that shorter contact throws more work on the second and third filters.

TABLE 46.—*Three-stage precipitation of low-grade mill solution with charcoal*

	Original loading		Total loading		Loading due to test		Precipitation (per cent)
	Milligrams	Ounces per ton	Milligrams	Ounces per ton	Milligrams	Ounces per ton	
Silver:							
First charcoal	12.38	180	21.15	308	8.77	128	33.0
Second charcoal	3.34	49	15.73	229	12.39	181	46.6
Third charcoal	.0	.0	5.40	79	5.40	79	20.3
Tail solution					.03		.1
Total					26.59		100.0
Gold:							
First charcoal	.16	2.3	.45	6.6	.29	4.2	96.7
Second charcoal	.04	.6	.05	.7	.01	.1	3.3
Third charcoal	.0	.0	Trace.	.0	Trace.	.0	.0
Tail solution					Trace.		
Total					.30		100.0

To ascertain the effect of passing a greater amount of solution through the filters, the preceding test was duplicated, with the exception that 7,200 cubic centimeters of the diluted mill solution was passed through the filters. The preliminary loading gave 13.01 milligrams silver, equal to a load of 190 ounces per ton, and 0.16 milligram gold, equal to a load of 2.3 ounces per ton, for the first charcoal; and 3.37 milligrams silver, equal to a load of 49 ounces per ton, and 0.04 milligram gold, equal to a load of 0.6 ounce per ton, for the second charcoal.

The average rate of filtration maintained was 1.14 centimeters per minute, or a contact period of 1 minute in each filter. At this rate 0.64 square foot of filter area would be required in each filter to precipitate 1 ton of solution per 24 hours. From the results given in Table 47, it is evident that the capacity of the filter had been passed or that the rate of filtration was too rapid.

TABLE 47.—*Three-stage precipitation of low-grade mill solution with charcoal*

	Original loading		Total loading		Loading due to test		Precipitation (per cent)
	Milligrams	Ounces per ton	Milligrams	Ounces per ton	Milligrams	Ounces per ton	
Silver:							
First charcoal	13.01	190	33.62	490	20.61	300	26.2
Second charcoal	3.37	49	30.07	439	26.70	389	34.0
Third charcoal	.0	.0	26.35	384	26.35	384	33.5
Tail solution					4.91		6.3
Total					78.57		100.0
Gold:							
First charcoal	.16	2.3	1.00	14.6	.84	12.3	97.7
Second charcoal	.04	.6	.06	.9	.02	.3	2.3
Third charcoal	.0	.0	Trace.	.0	Trace.	.0	.0
Tail solution					Trace.		
Total					.86		100.0

The results of these three tests of three-stage precipitation indicate that a contact period of only one minute in each filter is too short. With a larger volume of solution the load increased in the first charcoal, but the precipitation was evidently so slow that the second and third filters had more work than they could do. A slower rate of filtration or the use of a fourth filter would undoubtedly help this condition.

A comparison of the tests in this section shows clearly that three-stage precipitation is far more effective than agitation. It gives better results with less charcoal and a shorter time of contact.

Results of three-stage precipitation tests of this mill solution with sodium sulphide used as a fixer for the silver are given later.

SUMMARY

Agitation tests of synthetic and of mill solutions and three-stage precipitation tests of mill solutions show that better precipitation is obtained in three-stage precipitation with less time of contact and with less charcoal.

A comparison of the three-stage precipitation tests shows that the filtration rate should not be too fast, and that more than three-stage filtration might be advisable to obtain maximum loads on charcoal.

"FIXING" ADSORBED GOLD AND SILVER ON CHARCOAL

Tests were made to determine the possibility of so treating a loaded charcoal that the adsorbed substance would change its condition and remain in the charcoal unadsorbed, thus giving the charcoal the power to adsorb a new load. To this change of form the term "fixing" has been applied. The possibility presents itself of carrying a cycle of such operations to the point where the pores would be filled. Pulverized pine charcoal, which has a pore space of about 80 per cent, has a large interior space for storage.

To assume that the fixed metal must be left in a form insoluble in cyanide solution seems reasonable. If the metal were soluble, it would immediately be dissolved by the solution and readsorbed, with no possibility of the metals from the new solution being adsorbed.

REHEATING LOADED CHARCOAL FOR FURTHER PRECIPITATION

Statements (20, 22, 51, 52, 55) have been made that a loaded charcoal has its power of precipitation restored by heating. This change, if real, would be the result of fixing. The probability, however, is that aurous cyanide or argentous cyanide, or metallic gold or silver would be formed by the heating, would dissolve in free cyanide and be readsorbed, and the charcoal would be in the same condition as before heating.

A test in which pine charcoal was given a 24-hour contact with the solution, then heated red-hot for 15 minutes, cooled, and again given a 24-hour contact with a similar solution, heated again as before and given a 48-hour contact with a similar solution resulted in a final load much less than that obtained in one precipitation with a charcoal properly heat treated. The results indicated that a fourth treatment would have resulted in no further addition to the load.

SODIUM SULPHIDE AS A FIXER FOR SILVER

Sodium sulphide was studied as a fixer for silver because silver sulphide is not easily soluble in a cyanide solution. In the first test in which sodium sulphide was used, 1 gram of 100-mesh pine charcoal was given four cycles of treatments, each of which consisted of a half-hour contact with 100 cubic centimeters of sodium argentocyanide solution containing no free cyanide or alkalinity, filtering off and washing the charcoal, passing 50 cubic centimeters of one-half of 1 per cent sodium sulphide solution through the charcoal in the filter, and washing the charcoal once. Then charcoal was used in the second cycle.

Since a final load of 1,032 ounces silver per ton of charcoal was obtained in this test, with no indication that the limit had been reached, another test was made with more cycles of treatment.

In the second test the silver solution and 1 gram of pine charcoal were prepared and used as in the first test. For the sulphide treatment, 10 cubic centimeters of one-half of 1 per cent sulphide solution were passed through the charcoal twice, the charcoal washed once and transferred to the next 100 cubic centimeters of silver solution. Ten precipitations were made. The final charcoal, each tail solution, and the combined sulphide solutions were assayed; no soluble sulphides were found in the solutions. The results of this test, given in Table 48 and plotted in Figure 9, indicate a steady increase of load, leading to the conclusion that a very high silver capacity is obtainable on charcoal by the use of sulphide as a fixer.

TABLE 48.—*Using sodium sulphide as a fixer for silver in charcoal*

Precipitation	Milligrams silver in—			Individual results		Cumulative results	
	Charcoal	Solution	Total	Precipitation (per cent)	Load (ounces per ton)	Precipitation (per cent)	Load (ounces per ton)
First	15.78	9.40	25.18	62.7	460	62.7	460
Second	10.45	14.72	25.17	41.5	305	52.1	765
Third	13.27	11.91	25.18	52.7	387	52.3	1,152
Fourth	10.07	15.10	25.17	40.0	294	49.2	1,446
Fifth	6.62	18.56	25.18	26.3	193	44.6	1,639
Sixth	10.09	15.08	25.17	40.1	294	43.9	1,933
Seventh	7.80	17.38	25.18	31.0	227	42.0	2,161
Eighth	7.97	17.20	25.17	31.7	232	40.7	2,393
Ninth	7.40	17.78	25.18	29.4	216	39.5	2,609
Tenth	8.38	16.79	25.17	33.3	244	38.9	2,853
Sulphide solution		1.19	1.19				
Total	97.83	155.11	252.94				

A test in which a 0.05 per cent sulphide solution was used instead of a 0.5 per cent solution showed no beneficial effect whatever from the sulphide treatment.

Further study of the effect of sodium sulphide as a fixer showed that under certain conditions the tail solutions were dark colored because of unfiltratable silver sulphide. It was found that this could be prevented by a protective lime alkalinity in the solution. It was also found that a rather close control of the sodium sulphide was necessary. An excess of sodium sulphide causes soluble sulphides to appear in the tail solutions. A deficiency of sodium sulphide results not only in no precipitation, but also in the solution of a part of what has been precipitated.

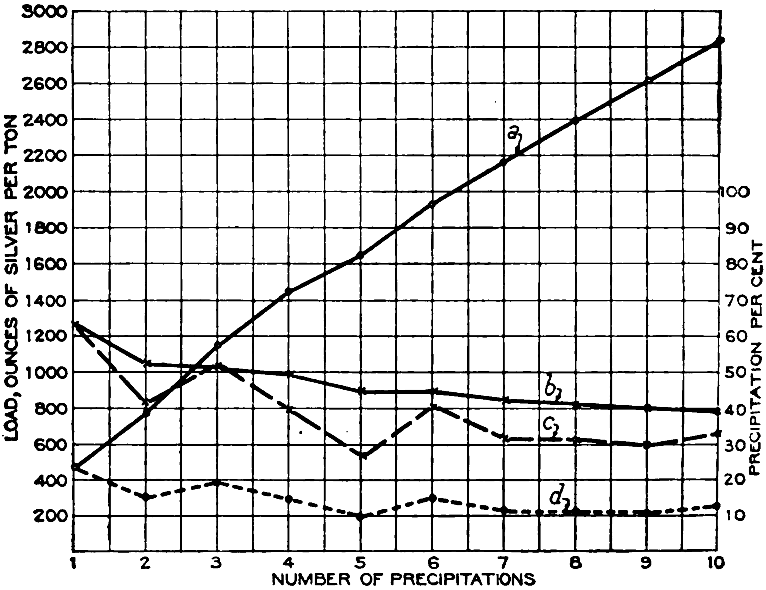

FIGURE 9.—Sodium sulphide as a fixer for silver on charcoal: *a*, Cumulative load; *b*, cumulative precipitation; *c*, individual precipitation; *d*, individual load

Sulphide as a fixer in stage precipitation.—Several tests were made with sodium sulphide as a fixer in the three-stage precipitation of a mill solution. The filters used were the same as those in the tests described previously. The solution used assayed 3.32 ounces of silver and 0.04 ounce of gold, with 0.35 pound KCy and 0.1 pound protective alkalinity per ton.

By using 50-mesh pine charcoal with six precipitation cycles, in each of which 400 cubic centimeters of the mill solution were passed through the filters under low vacuum and were followed by 2 cubic centimeters of 1½ per cent sulphide solution, a load of 1,869 ounces of silver per ton was obtained on the first charcoal, with precipitation of 81.7 per cent of the silver and 99 per cent of the gold. The contact period in each filter was one-half minute.

Since the results of this test suggested the possibility of a much greater load, a test was made in which 20 precipitation cycles were given as before, but various changes in the sulphide treatment were made.

Gravity filtration was used to allow a longer contact between solution and charcoal. The charcoal used had been pulverized to pass a 50-mesh sieve, and all that was finer than 300-mesh was removed to assist filtration. Two grams of charcoal were used in each filter, but because of the removal of the fines, the filter bed had a depth of 1.4 inches. The coarse charcoal seemed unable to hold an excess of sulphide solution and allowed it to pass through the last filter; not until the amount of sulphide was reduced to the theoretical amount required to convert the silver to sulphide were the tail solutions clear and colorless. The time of contact between solution and charcoal was five minutes in each filter. The silver and gold in the three charcoals at the end of the test were distributed as follows: The first charcoal contained 73.1 per cent of the silver and 45.4 per cent of the gold; the second charcoal contained 19.2 per cent of the silver and 18.6 per cent of the gold; the third charcoal contained 7.7 per cent of the silver and 36 per cent of the gold.

TABLE 49.—*Using sodium sulphide as a fixer with mill solutions*

Precipitation	Milligrams metal in—			Precipitation (per cent)		Cumulative load on—		
	Charcoal	Solution	Total	Individual	Cumulative	First charcoal	Second charcoal	Third charcoal
Silver:								
1-2 [1]	87.05	0.67	87.72	99.2	99.2	928	244	98
3-4 [1]	80.92	6.80	87.72	92.2	95.7	1,790	471	188
5-6 [2]	73.47	14.25	87.72	83.8	91.7	2,573	677	270
7-8 [3]	67.39	20.32	87.71	76.8	88.0	3,291	866	346
9-10 [4]	59.84	27.87	87.71	68.2	84.1	3,929	1,034	413
11-12 [5]	54.34	33.37	87.71	62.0	80.4	4,508	1,187	474
13-14 [6]	35.25	52.46	87.71	40.2	74.6	4,884	1,285	514
15-16 [7]	39.57	48.14	87.71	45.1	70.9	5,305	1,397	558
17-18 [8]	46.38	41.33	87.71	52.9	68.9	5,799	1,527	610
19-20 [8]	47.13	40.58	87.71	53.7	67.4	6,302	1,659	663
Total	591.34	285.79	877.13					
Gold:								
1-2 [1]	1.04	Trace.	1.04	100.0	100.0	6.9	2.8	5.5
3-4 [1]	1.03	0.01	1.04	99.0	99.5	13.7	5.6	10.8
5-6 [2]	.78	.26	1.04	75.0	91.5	18.9	7.7	14.9
7-8 [3]	.54	.50	1.04	51.9	81.5	22.4	9.2	17.8
9-10 [4]	.00	1.04	1.04	.0	65.2	22.4	9.2	17.8
11-12 [5]	.49	.55	1.04	47.1	62.2	25.7	10.5	20.3
13-14 [6]	.56	.48	1.04	53.8	61.0	29.4	12.1	23.3
15-16 [7]	.74	.29	1.03	71.8	62.3	34.3	14.1	27.2
17-18 [8]	.45	.58	1.03	43.7	60.3	37.3	15.3	29.5
19-20 [8]	.54	.49	1.03	52.4	59.5	40.8	16.8	32.4
Total	6.17	4.20	10.37					

---

[1] Two cubic centimeters of 1½ per cent sodium sulphide solution added to first 30 cubic centimeters of mill solution in filter.

[2] Two cubic centimeters of 1½ per cent sodium sulphide solution directly on charcoal before mill solution.

[3] One and a half centimeters of 1½ per cent sodium sulphide solution directly on charcoal before mill solution.

[4] CaO added to mill solution (0.25 lbs. P. A.), sodium sulphide solution as in (1).

[5] Two cubic centimeters of 1½ per cent sodium sulphide solution directly on charcoal one-half hour before mill solution in first precipitation; no sulphide in second precipitation.

[6] One cubic centimeter of 1½ per cent sodium sulphide solution added to first 30 cubic centimeters of mill solution in filter.

[7] Three-fourths cubic centimeter of 1½ per cent sodium sulphide solution directly on charcoal 15 minutes before mill solution.

[8] One cubic centimeter of 1½ per cent sodium sulphide solution directly on charcoal before mill solution.

The results in Table 49 are based on the assumption that in each precipitation the distribution of the metals in the three filters was the same as at the end of the test. The tail solutions from two successive precipitations were combined for assay; the results are, therefore, the results of 10 double precipitations.

It is interesting to note the effect of the sulphide in carrying the gold, because of its solubility in the sulphide, through the filters. This effect is especially noticeable when stronger solutions of sulphide were used and the precipitation of gold quickly fell to zero.

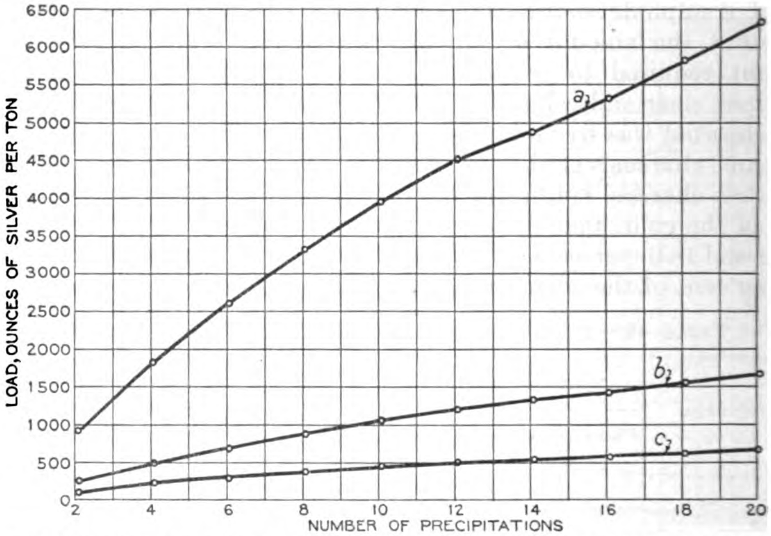

Figure 10.—Silver loads obtained on charcoal from mill solution by using sodium sulphide as a fixer: *a*, Cumulative load, first charcoal; *b*, cumulative load, second charcoal; *c*, cumulative load, third charcoal

The cumulative curves of this test (fig. 10) show that the ultimate load of the charcoals had not been reached, and that apparently they could have been loaded to much greater capacity.

In general, the motive for using sodium sulphide with the charcoal is that if a slight excess of the sulphide be used, it will be retained in the charcoal and will not contaminate the solution; or, if a slight deficiency be used, the precipitation is completed by the adsorptive power of the charcoal.

SULPHURETED HYDROGEN AS A FIXER FOR SILVER

Sulphureted hydrogen was tried as a fixer in the precipitation of silver, but the results were not favorable. One gram of 70-mesh pine charcoal was used for a series of six precipitations. The charcoal was given a half-hour contact with the silver solution, which contained no free cyanide or alkalinity, treated between each precipitation by passing sulphureted hydrogen through it for a period of 10 minutes, then washed and used again for the succeeding precipitation. The results indicated that sulphureted hydrogen did not act as a fixer as did sodium sulphide.

NITRIC ACID AS A FIXER FOR GOLD AND SILVER

The effect of nitric acid as a fixer for both silver and gold was investigated by several tests in which 1 gram of 70-mesh pine charcoal was used with 100 cubic centimeters of solution, and a half-hour contact was given. The charcoal was then filtered, washed twice, and given 15 minutes' contact with 10 cubic centimeters of 1 per cent nitric acid (by volume), again filtered, washed twice, and used in the next precipitation. The results of a number of tests showed that if the charcoal is dried after the nitric treatment, the results are not as good as when it is not dried.

The tests usually gave somewhat erratic results; those of only two tests are given in Table 50. In these tests the solutions contained 1 pound KCy per ton and the charcoal was not dried after the acid treatment. These results show that although the load ordinarily obtainable is increased 50 per cent, the effect of the nitric acid treatments rapidly diminishes.

TABLE 50.—*Results of using nitric acid as a fixer for silver and gold in charcoal*

Precipitation	Milligrams metal in—			Individual results		Cumulative results	
	Charcoal	Solution	Total	Precipitation (per cent)	Load (ounces per ton)	Precipitation (per cent)	Load (ounces per ton)
Silver:							
First	12.63	11.22	23.85	53.0	368	53.0	368
Second	18.03	5.82	23.85	75.6	526	64.3	894
Third	8.81	15.04	23.85	36.9	257	55.2	1,151
Fourth	2.35	21.50	23.85	9.8	69	43.8	1,220
Fifth	1.98	21.87	23.85	8.3	58	36.7	1,277
Sixth	.94	22.91	23.85	3.9	27	31.3	1,305
Seventh	1.15	22.70	23.85	4.8	34	27.5	1,338
Eighth	4.07	19.77	23.84	17.1	119	26.2	1,457
Nitric acid solution	---------	.19	.19	---------	---------	---------	---------
Total	49.96	141.02	190.98	---------	---------	---------	---------
Gold:							
First	30.68	8.63	39.31	78.0	895	78.0	895
Second	32.95	6.36	39.31	83.8	961	80.9	1,856
Third	16.59	22.72	39.31	42.2	484	68.0	2,340
Fourth	7.74	31.57	39.31	19.7	226	55.9	2,565
Fifth	3.15	36.16	39.31	8.0	92	46.3	2,657
Sixth	2.42	36.89	39.31	6.2	70	39.7	2,728
Seventh	1.31	38.00	39.31	3.3	38	34.5	2,766
Eighth	.91	38.39	39.30	2.3	27	30.4	2,793
Nitric acid solution	---------	.72	.72	---------	---------	---------	---------
Total	95.75	219.44	315.19	---------	---------	---------	---------

HYDROCHLORIC ACID AS A FIXER FOR GOLD

The effect of hydrochloric acid as a fixer for gold was also investigated. Six precipitation cycles were used, in which 200 milligrams of charcoal were given a half-hour contact with 100 cubic centimeters of gold solution, then filtered, washed, and given from 5 to 25 minutes' contact with 100 cubic centimeters of 1 per cent (by volume) hydrochloric acid solution, again washed, and added to the next gold solution. This procedure gave no beneficial results, since the precipitation obtained was not more than that without hydrochloric acid treatment.

SUMMARY

The term "fixing" has been applied to such treatment of loaded charcoal as causes a change of the adsorbed substance and leaves the charcoal free to take on another load.

Reheating a loaded charcoal did not restore its adsorptive power.

With a sodium sulphide treatment the capacity of a silver-loaded charcoal was easily increased sixfold. The controlling factor seems to be the amount of sulphide used.

Sulphureted hydrogen did not prove effective as a fixer for silver.

With nitric acid as a fixer the capacity of charcoal for both gold and silver was increased about 50 per cent.

Hydrochloric acid had no effect as a fixer for gold.

FLOTATION OF CHARCOAL FROM AN ORE PULP

A test was made to determine whether the soluble gold and silver might be recovered from a mixture of ore and cyanide solution by adding pulverized charcoal and then recovering the charcoal by flotation.

Flotation has been suggested for the removal of carbonaceous matter from an ore pulp (65, 96). The flotation of charcoal added to an ore pulp is simpler than the flotation of carbonaceous matter forming an integral part of the ore.

In order to select a satisfactory flotation agent, experiments were made on the flotation of charcoal from a cyanide solution that did not contain ore. A satisfactory froth was obtained, and 91.6 per cent of the charcoal was floated with two parts xylol and one part hardwood creosote. The charcoal must be added to the pulp and enough agitation given to obtain precipitation before the oil is added, as the latter coats the charcoal and makes it unfit for precipitation. This fact forms a basis for the treatment of carbonaceous ore (96).

Two tests were made with an ore pulp of 750 grams of oxidized silver ore pulverized to pass a 70-mesh sieve, and 3,000 cubic centimeters of 1.8 pounds cyanide solution. Lime equal to 10 pounds per ton of ore was used. In one test 15 grams of 100-mesh pine charcoal (40 pounds per ton of ore) were added to the pulp just after the ore was mixed with the cyanide solution. After 48 hours' agitation the pulp was floated in a Ruth machine by the use of 3.2 pounds xylol and 2 pounds of Cleveland Cliffs creosote No. 1 per ton of ore. In the second test no charcoal was added. At the end of 48 hours' agitation the pulp was floated with the same amounts of oil to see what effect flotation had on the ore itself. In each test the froth and tailing were filtered, washed, dried, and assayed. The solutions from the froth and tailing were combined and assayed. Only silver assays are given; the ore contained practically no gold. The results appear in Table 51.

TABLE 51.—*Flotation of charcoal from an ore pulp*

Product	Test containing charcoal			Test without charcoal		
	Weight (grams)	Assay (ounces per ton)	Contents (milligrams)	Weight (grams)	Assay (ounces per ton)	Contents (milligrams)
Froth	41.5	127.64	181.60	37.5	2.00	2.57
Tailing	708.5	2.88	69.96	712.5	2.78	67.91
Solution			82.72			263.42
	750.0	13.00	334.28	750.0	12.99	333.90

The silver on the charcoal in the froth was $181.60-2.57=179.03$ milligrams; the silver on the charcoal in the tailing was $69.96-67.91=2.05$ milligrams; the total silver precipitated on the charcoal was $263.42-82.72=180.70$ milligrams; the precipitation, therefore, on the charcoal was $\frac{263.42}{180.70}\times 100=68.6$ per cent. The charcoal floated was $\frac{179.03}{179.03+2.05}\times 100=98.9$ per cent. The load obtained on the charcoal was 352 ounces of silver per ton. As pine charcoal in a clean solution could have precipitated all the silver, there seems to have been an interference by the pulp. The test shows, however, the possibility of precipitation in the pulp and of floating the charcoal, as a fairly clean product, almost completely away from the pulp.

COMMERCIAL APPLICATION OF CHARCOAL PRECIPITATION

The objections to charcoal as a precipitant are: (1) Its bulk and the weight required, especially for silver; (2) the loss of cyanide due to its adsorption by the charcoal; and (3) the nuisance of burning the charcoal for a clean-up. Charcoal as a precipitant has advantages that might well be utilized under certain conditions that are discussed on a later page.

In the precipitation of gold and silver by charcoal from cyanide solutions, only a bicarbonate enters the solution, which is consequently in as good a condition for further dissolving as at first. Charcoal is, therefore, a clean precipitant, and does not contaminate the solution with harmful substances.

That charcoal precipitates copper from a cyanide solution (22, 28, 37, 66) was verified. Therefore, a mill solution, if its copper content were not too great, would be kept free from copper by the use of charcoal as a precipitant.

When charcoal is used as a precipitant from cyanide solution, very few fouling agents affect the precipitation seriously; some even seem to assist it. From a cyanide solution containing picric acid the gold could not be precipitated by zinc but was readily precipitated by charcoal.

Charcoal is comparatively cheap and its preparation is not difficult. Any wood is satisfactory, though the softer woods are preferable. In burning the charcoal the temperature must be high enough and the time long enough. Oxidation must accompany the heating. Pulverization, either wet or dry, is necessary, but this need not be carried to such a degree of fineness as to prevent gravity filtration.

IN A SMALL ISOLATED PLANT

A small isolated plant having wood available could employ charcoal in preference to zinc, especially for precipitating gold. Three-stage gravity filtration with fairly coarse charcoal could be done at low cost. Undue losses of cyanide could be prevented by arranging the flow sheet so that solutions low in cyanide would be precipitated. The loaded charcoal could be shipped to a smelter (this would be no more difficult than shipping the zinc-box product, which was often done in the early days of cyanidation) or the charcoal could be burned and the ash melted down to bullion. The burning of the charcoal must be done carefully to avoid dust loss; this loss could perhaps be largely prevented by impregnating the charcoal with sodium carbonate before burning, for the authors noted that when charcoal had been impregnated with soda ash or caustic soda it burned quietly without tendency to dust.

PRECIPITATION OF FOUL SOLUTIONS

Charcoal could replace zinc when foul solutions cause trouble in precipitation (61, 62, 63, 66), as few fouling agents seem to have any serious effect in charcoal precipitation.

PRECIPITATION OF WASTE SOLUTIONS

Charcoal is an excellent precipitant for small amounts of gold or silver from waste solutions containing little or no free cyanide (17, 43, 93). Charcoal with a high load capacity is not as necessary here as are simplicity of operation, efficient precipitation, and low expense—all of which requirements charcoal meets.

Gravity filtration through beds of charcoal, not pulverized too fine, in stage precipitation requires only the occasional removal of the head filter and the addition of a fresh tail filter. The lack of free cyanide in the solution is a distinct advantage in charcoal precipitation. A three-stage charcoal filter would probably be ample for complete precipitation.

Charcoal precipitation can be applied as an auxiliary to the regeneration of cyanide by means of acid. When the solution is acidified, all the silver is readily precipitated, but owing to the slow formation of the aurous cyanide, only a part of the gold is precipitated. The solution, after the removal of hydrocyanic acid and the precipitate, is free from cyanide, and is either neutral or slightly acid. The gold is in ideal condition for complete precipitation on charcoal, and the precipitation occurs so rapidly as to seem instantaneous. A single or, at most, a double stage filter should prove satisfactory, and gravity filtration can be used if the charcoal is rather coarsely pulverized.

PRECIPITATION IN AN ORE PULP

If a cyanide ore pulp still containing precious metals in soluble form is going to waste, the gold and silver may be precipitated by adding pulverized charcoal, agitating, and then recovering the charcoal by flotation. With this method no filtration of the pulp is necessary.

NECESSITY OF INCREASING CHARCOAL CAPACITY

The serious disadvantage in the use of charcoal to precipitate gold and silver, especially silver, from a cyanide solution, lies in the large volume of precipitants that must be handled. To illustrate this point two examples of charcoal requirement are given:

1. A mill treating 100 tons of ore containing $10 of recoverable gold per ton would require 1 ton of charcoal per month, if the charcoal were loaded to 1,500 ounces—a fair load. This weight of pine charcoal pulverized to 50-mesh would occupy wet about 90 cubic feet.

2. A mill treating 100 tons of ore containing 10 ounces of recoverable silver per ton would require 40 tons of charcoal per month, if the charcoal were loaded to 750 ounces—a fair load. As this requirement would necessitate burning over 100 cubic feet of charcoal daily, one can see that if charcoal is to have a broad application in cyanidation, its capacity must be increased manyfold. The problem of obtaining increased capacity can be attacked from three different points:

Increased capacity by activation.—As the limit of capacity is a monomolecular layer or, with pine charcoal, about 8,800 ounces of gold or 5,880 ounces of silver per ton, the possibility of producing activated charcoal that could be generally used in cyanidation is not promising. Such a charcoal when fully loaded would contain 23 per cent of gold but only 17 per cent of silver before burning—not an attractive outlook for silver precipitation. In no tests were results obtained to indicate that such capacities could be reached by activation of the charcoal.

Dissolving the adsorbed gold and silver salts from charcoal and again using it.—If the adsorbed gold or silver salts were removed with a solvent, leaving the charcoal in condition to take on another load, the necessity of burning the charcoal would be obviated. Several solvents were found for the gold salt. Sodium sulphide (57, 66), which has no solvent action on the silver salt, proved the most efficient of the substances tried. Tests indicate, however, that the amount dissolved by the sulphide decreases after the first treatment. For the silver salt, mercurous nitrate, which has no solvent action on the gold salt, was found most efficient, but its cost makes it of no practical value.

The best solvents for the adsorbed salts of both gold and silver were found to be sodium hydroxide, hot water, and cyanide. A 1 per cent sodium hydroxide solution dissolved 11 per cent of the gold salt and 13 per cent of the silver salt at room temperature, and 50 per cent of the gold salt and 61 per cent of the silver salt at boiling temperature; with boiling water, 28 per cent of the gold salt and 24 per cent of the silver salt were dissolved. A 1 per cent cyanide solution dissolved 17 per cent of the gold salt and 32 per cent of the silver salt at room temperature, and 65 per cent of the gold salt and 86 per cent of the silver salt at boiling temperature. By passing through the loaded charcoal a boiling cyanide solution containing 2 pounds of cyanide per ton, 62.7 per cent of the gold salt and 95.4 per cent of the silver salt were removed.

The disadvantage of dissolving the adsorbed salts in order to reuse the charcoal is that the metals must again be precipitated from the solvent which, however, would be highly concentrated.

Treating loaded charcoal to renew its precipitating power.—Treating a loaded charcoal with some reagent that will "fix" the adsorbed salt, leaving it in the charcoal and renewing its precipitating power, would give increased capacity.

By three-stage precipitation on a mill solution, with 50-mesh charcoal and sodium sulphide as a fixer, a silver load of 6,300 ounces per ton was obtained and the limit had apparently not been reached.

An advantage of sulphide fixing is that all the cyanide seems to be regenerated.

Other substances tried as fixers were as follows: Sulphureted hydrogen for silver—not promising; hydrochloric acid for gold—no action; and nitric acid for gold and silver—promising, as a 50 per cent greater load of gold and silver was obtained on 70-mesh charcoal than could be obtained without nitric acid fixing on 200-mesh charcoal.

As the fixing of gold and silver on charcoal has been studied to a small extent only, few substances have been tried. From the results obtained fixing seems a promising method for obtaining large loads on charcoal.

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